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A holistic zero waste biorefinery approach for macroalgal biomass utilization: A review

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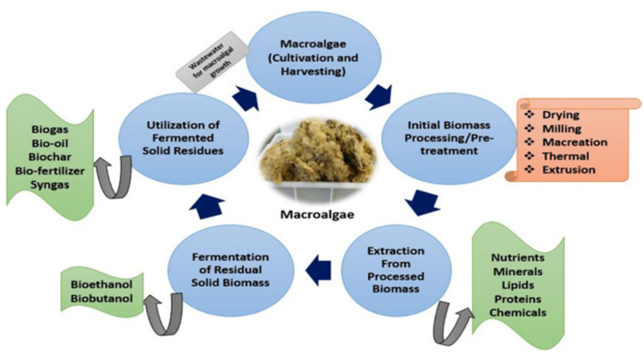
HIGHLIGHTS

- Macroalgae contains a diverse range of polysaccharides with little or no lignin.
- Macroalgae has high photosynthetic rate and biomass production potential.
- Hydrolysis and fermentation play a key role in macroalgal bioethanol production.
- Scaling up studies on bioethanol production from macroalgae is scarce.
- High potential of macroalgae towards a holistic zero waste biorefinery

GRAPHICAL ABSTRACT



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ABSTRACT

The growing concerns over the depleting fossil fuels and increase in the release of greenhouse gas emissions have necessitated the search for the potential biomass source for alternative energy generation. In this context, third generation biomass specifically maroalgae has gained a lot of research interest in the recent years for energy and products generation such as ethanol, butanol, alginates, agars, and carrageenans. There are a few reviews available in scientific domain on macroalgal biomass utilization for bioethanol production but none of them has addressed precisely from phenolic precursor compounds to the entire ethanol production process and its bottlenecks. Here, we explained critically the processes involved in bioethanol, value added products and chemicals production utilizing macroalgal biomass as a feedstock along with its zero waste feasibility approach. Apart from this, we have also summarized the major issues linked to the macroalgae based biofuels and bioproducts generation processes and their possible corrective measures. Biorefinery is a promising way to generate multiple products from a single source with short processing time. Thus, this review also focuses on the recent advancement in the macroalgal biomass scaling up and how this could help in the growth of macroalgal biorefinery industry in the near future.

1. Introduction

The current advancement in the cutting edge technologies with new energy and environment policies have resulted in the expansion of energy markets globally. Such expansion further necessitates the

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requirement of biomass based energy to compensate the upsurging energy demand (International Renewable Energy Agency, 2019). The prime contribution of biomass in energy sector is that it inherits a hidden vast pool of energy rich precursors that can be transformed into an array of biofuels and biocommodities. There is an intensified growth in energy demand from many decades which is mainly being satisfied by the fossil fuels. The future energy scenarios for industries will be different because of the emergence of disruptive trends. Such type of development led to a fundamentally new world represented by more environmental issues, new technologies and a shift in biomass energy sector (World Energy Scenarios, 2019). Continuous energy generation from the fossil fuel reserves not only exhausted these finite resources, but also gradually polluted the environment that has resulted in unprecedented climatic changes (Owusu and Asumadu-Sarkodie, 2016). Thus, there is an immense need to explore the viable biomass feedstock for sustainable supply of energy against the demand.

During the last decade, biofuels and other biochemicals have been produced mainly from food and non-food biomass to meet the energy demand (European Union Biofuels Annual, 2018). The utilization of first generation biomass such as sugarcane, corn and sorghum for biofuels production has led to the food, fodder and fuel issues. Such type of practice not only capture the productive agricultural land that involved in food production but also resulted in the transformation of arable land to non-arable because of the deforestation and regular use of fertilizers (Groom et al., 2008; Searchinger et al., 2008; Naik et al., 2010). Even though some countries like USA and Brazil still use first generation based fuels (corn based), for most countries (especially India, Korea and some South East Asian countries) the problem is still inevitable due to food vs. fuel debate. Lignocellulosics (second generation biomass) and seaweeds (macroalgae, third generation biomass) act as a potent biomass blueprint for the production of an array of biofuels and chemicals (Suganya et al., 2016). The major limitations for lignocellulosic biofuels production are the presence of complex aromatic structure called lignin that hinders the accessibility of cellulose and hemicellulose molecules (Martín-Sampedro et al., 2013).

Compared to the lignocellulosic terrestrial biomass, seaweeds are characterized with no or low amount of lignin (Wi et al., 2009; Ge et al., 2011). Thus, lignin degradation or removal is not needed for seaweeds and which further simplify the conversion process of carbohydrates contained in marine biomass into biofuels and chemicals. Moreover, seaweeds cultivation does not require cultivable agricultural land. Both macroalgae and microalgae have the potential to produce a broad range of high value products apart from fuel itself. Moreover, their role in biofuel market as a promising candidate for biodiesel and bioethanol has been growing dramatically (Suganya et al., 2016). Microalgae due to their high lipid content is mainly suitable for biodiesel production, whereas macroalgae because of high carbohydrate content is explored for bioethanol generation (Suganya et al., 2016; Kumar et al., 2019). Based on these features, algae biomass can be a promising feedstock for a zero waste conversion technology that directs towards the production of biofuels and other value added products. A zero waste approach is a sustainable process that can recycle, reduce or reuse the solid-liquid waste obtained from a production process (Mishra et al., 2019). Due to its broad spectrum production strategy, it has several advantages over conventional approaches. It minimizes the dependency on fossil fuels, diversifies the biobased resources, reduces emission of greenhouse gases, and protects the natural environment by stimulating greener development of rural and regional areas (Arevalo-Gallegos et al., 2017). There are a few reports on the production of pharmaceuticals, food and other valuable products that describes the zero waste potential of macroalgal biorefinery (Mhatre et al., 2019; Zollmann et al., 2019; Sadhukhan et al., 2019; Ingle et al., 2018; Nunes et al., 2018).

The biorefinery approach describes the production of energy, specialty chemicals and other value added products under a common platform (Bikker et al., 2016). The recent advances in biorefinery includes the joint operations of technologies and processes for biomass conversion to food, energy, feed and other valuable products that help to develop a commercially viable industrial economy and minimize the impact on climate change (Balina et al., 2017). The usefulness of the biorefinery approach lies on the principle of biomass exploitation at each and every process step with minimum waste generation. However, if all the process leftovers (solid and liquid waste) were further utilized efficiently for by-products generation, a zero waste production might be possible (Balina et al., 2017). The waste generated from macroalgal biofuel conversion process can be broadly classified as solid residue and liquid effluent. Such type of wastes contain a significant quantity of nutrients and can be further used for the production of other forms of energy and value added products (Gifuni et al., 2019).

The prime goal of this review is to provide insights to the scientific community regarding the current research on macroalgal based biofuels and bioproducts along with the recent developments and challenges. Furthermore, different macroalgal biomass hydrolysis and fermentation methods for ethanol generation have been discussed. Moreover, the review also detailed about the macroalgal biomass scaling up for biofuels production that describes about the feasibility of the process for commercialization.

2. Methodology

We have performed a systematic observation based literature search pertaining to macroalgal biomass utilization for biofuels and bioproducts production. We targeted mainly on macroalgal species employed for fuels and products formation in Web of Science (mjl.clarivate.com/search-results) by using the keywords ("macroalgae + bioenergy"). No other filtering criteria such as publication date or language were considered. This results in total of 10 master list of journals that contains the information on macroalgae based biorefinery approach for biofuels and bioproducts generation. We further went through the research as well as review articles that belong to the master list of journals to extract the literature regarding utilization of macroalgae for valuable products generation. Apart from this, we have also searched in Google Search Engine by using the keywords ("macroalgae + production + cultivation"). This gives a total of 5150 articles. We have screened those articles which are not fitting to our criteria as detailed below: 1) No mention of production, cultivation, and harvesting of macroalgae; 2) No literature on characteristics of macroalgae; 3) No information on occurrence of different structural polysaccharides in macroalgae. In addition, keywords ("macroalgae + biorefinery") was also used in Google Search Engine that gives a total 78,200 results. Further we have excluded those articles which are not fitting to our criteria as detailed below: 1) No information on macroalgal biomass utilization for biofuels and products generation; 2) No detailed literature regarding challenges of the lignocellulosic biofuel production process. A total of 886,000 articles were found by using the keywords ("macroalgae + scaling up") and subsequently the articles were screened which are not fitting to our criteria as mentioned below: 1) No mention of scaling up process for bioethanol production utilizing macroalgal biomass; 2) Lack of information on scaling up of macroalgal biomass with policy support; 3) No measured ethanol concentration or productivity. We also performed supplementary search for the review on different aspects related to the issues and bottlenecks associated with macroalgal biofuels production process and downloaded about 30 such studies.

Reports on both biofuels and bioproducts generation from macroalgae are limited along with their commercial applications. Literatures on full utilization of macroalgal biomass through zero waste approach for products formation are rare. Therefore, this deficient venture is taken as a main theme for this review.

3. Sustainable production feasibility

3.1. Sustainable seaweed production

Sustainable production of seaweed is one of the main challenging tasks, since it is in early phase of aquaculture. Global production of seaweeds has been increased exponentially during the last five decades from 7 million tons to 24 million tons and still growing (Food and Agriculture Organization, 2016). Sustainable yield of seaweeds is further dependent on the types of geographical region and its weather conditions. Its farming is increasing with pace in some countries, while slowly gaining acceptance in others (Tiwari and Troy, 2015). Several authors have reported that seaweed aquaculture can yield billion tonnes of macroalgae per year which could offer a sustainable supply of biomass in the near future (Radulovich et al., 2015; Bjerregaard et al., 2016; Kim et al., 2017). Thus, round the year availability of macroalgal biomass makes it a promising candidate for energy and other value added products generation.

3.2. Enrichment of economic feasibility of macroalgae for biofuels production

Macroalgae can be employed for the production of biofuels. Apart from biofuel production, macroalgae helps to control pollution and act as a source of nutritional supplements. The major contribution of macroalgae for other useful purposes are described in Table 1.

Macroalgae can potentially reform the various sectors of biotechnology such as biofuels, food, cosmetics, pharmaceuticals and aquaculture due to its capability to produce high value biological products while minimizing the environmental pollution (Suganya et al., 2016).

3.3. High value co-product strategy

The economic feasibility of the macroalgae based biofuel production process should be improved significantly through a high value co-product strategy. This strategy is comprised of a sequential process that includes cultivation of macroalgae in farming facility, extraction of bioactive compounds from harvested macroalgal biomass, residual biomass conversion (hydrolysis, pyrolysis, fermentation, and liquefaction) for fuel generation followed by fermented or processed waste utilization towards low value-high volume products generation (Suganya et al., 2016). Trivedi et al. (2016) carried out a sequential extraction of different compounds such as 26% (*w*/w) mineral rich liquid extract, 2.8% (w/w) lipid, 25% (w/w) ulvan, and 11% (w/w) cellulose by using *Ulva fasciata* as a macroalgae feedstock. Similar type of co-product strategy was also reported by using *Ulva lactuca* as a substrate where mineral rich liquid extract, ulvan, protein and methane were extracted (Mhatre et al., 2019). Such kind of production strategy helps to reduce the biomass processing costs (Trivedi et al., 2016). Therefore, sequential production processes are profound to recommend for utilizing the maximum commercial potential of the macroalgae feedstock in a biorefinery point of view.

3.4. Strengthening the role of macroalgal biorefinery under the principles of bioeconomy

The development of bioeconomy not only depends on economic sectors and biorefinery end products but also is influenced by human resources, environmental, climate, technological and socio-economic aspects (Muizniece et al., 2016). The key principles of bioeconomy framed by European Commission are to assure sustainable use of biomass resources, to provide food security, to reduce impact on environment, and to ensure competitiveness (Mathijs et al., 2015). Macroalgal biorefinery can be adapted to the above key principles and contributes a major role in strengthening the bioeconomy.

3.5. Cascading approach for establishment of zero waste biomass utilization

The product generation process utilizing macroalgae as a feedstock is broad and it produces variety of end products by different methods. Cascading approach is a stepwise release of products from biomass with the high value product first followed by the second highest value product and so on. The major issue prevailing in the current situation is that large amount of edible and non-edible biomass meant for high value product generation is used to produce bioenergy and biofuels (Geldermann et al., 2016). The concept of macroalgal biorefinery has been developed in such a way that the high value product is produced first and thereafter, leftover residues were converted to low value products. Such type of approach increases the efficiency of resource utilization through zero waste generation and even adds more value to the utilized biomass. Furthermore, increased resource efficiency cut down the supply of raw feedstock due to its repeated use and helps to achieve zero waste biomass utilization approach (Balina et al., 2017).

3.6. Summary

Different aspects of macroalgae were considered that includes sustainable seaweed production, enhanced economic feasibility of macroalgae for biofuels and bioproducts generation, co-product strategy, and cascading approach for multi-product formation.

4. Global seaweed and macroalgae production status

The application of macroalgae, specifically brown seaweeds, for various products has been practiced since the early 20th century but its role along with green and red seaweeds in the field of energy generation has been considered recently (Bruton et al., 2009). The trend of seaweeds cultivation has grown in the recent years. Usually two types of seaweeds, red (57%) and brown (43%) are cultivated for energy and other value added products generation. Seaweed production increases worldwide up to 5.7% every year and around 30.4 million tons of seaweed were reported from global capture and culture sectors in 2015 (Food and Agriculture Organization, 2018). The value of the global seaweed industry is more than 6 billion USD per annum of which 85% comprises of food based products for human consumption (Food and Agriculture Organization, 2013).

Table 1
Major contributions of different types of macroalgal species.

Macrolagal species	Major contributions	Methodologies/process	Reference
Chaetomorpha linum Kutzing, *Pterocladiella capillacea*	Enhanced CO_2 fixation and biofuels production	Supercritical carbon dioxide extraction	(Aresta et al., 2005)
Kelp sp.	Wastewater treatment	Environment Protection Agency (EPA) methods for wastewater analysis 354.1, 375.4, 350.1	(Biris-Dorhoi et al., 2016)
Sargassum, *Gracilaria*, *Macrocystis pyrifera*, *Ulva lactuca*, *Laminaria* sp.	Methane production	Anaerobic digestion	(Barbot et al., 2016)
Ulva sp.	Biofertilizer production	Boiling	(Akila et al., 2019)
Ulva lactuca	Source for several bioactive compounds such as sugars, antioxidants, protein, lipids, and minerals	Heat treatment	(Gajaria et al., 2017)

Currently, the major leading seaweed production countries are China and Indonesia, producing more than 10 million tonnes individually, followed by Philippines and Republic of Korea, each contributed more than 1 million tonnes, while Japan, Malaysia and North Korea produced over 100,000 t each. In America, only Chile has reported to cultivate around 12,836 t of macroalgae *Gracilaria* (Buschmann et al., 2017).

The global production of macroalgae is approximately 6 billion USD and it consists of mainly food products for human consumption produced from aquaculture (Food and Agriculture Organization, 2014). Majority of the macroalgae producers were concentrated in the East and Southeast Asia and among them, the dominant candidates are China, Indonesia, Republic of Korea, Philippines, Japan and North Korea (Fig. 1) (Buschmann et al., 2017; Food and Agriculture Organization, 2016). In the recent decades, exploitation of macroalgae for biofuels production has gained momentum due to huge pressure on energy demand.

Undoubtedly, cultivation of macroalgae usually enhances primary production that includes food products and thus contributes to the global oxygen, carbon and various nutrient cycles apart from reducing release of greenhouse gases and eutrophication (Chung et al., 2011; European Commission, 2016). The commercial farming of macroalgae also offer several ecosystem services, namely food and habitat for an array of invertebrates and fishes of conservation importance (Almanza and Buschmann, 2013; Vásquez et al., 2014). Moreover, potential macroalgae strain selection is also a deciding factor for enhanced biofuels and biochemical production. Till now, most exploited macroalgae strain is *Laminaria japonica* followed by *Sargassum* spp. This is because both species have traditional food value and cultivated extensively in East Asian countries (Mazarrasa et al., 2014). Worldwide around 221 macroalgae species are used currently by humankind for food and other products generation (Pereira, 2011). However, maximum macroalgal biomass is derived from a relatively few species belonging to genera *Laminaria*, *Gracilaria*, *Euchema*, *Porphyra*, and *Undaria* (Roesijadi et al., 2010; Murphy et al., 2013). Carbohydrates act as the major compounds in biofuels production process and are also important in biorefinery point of view (Adams et al., 2011). Kelp or brown macroalgae is known to contain maximum carbohydrates (60%, dry weight) compared to other species of macroalgae (Kraan, 2013). It was reported that brown macroalgae showed variation in seasonal compositional carbohydrate content which is high during autumn and low in winter. Thus, this can be beneficial for biofuel refineries for yield maximizing of targeted compound and minimizing low value compounds (Schiener et al., 2014).

In addition, macroalgal species employed for non-fuel purpose might not be suitable for conversion to biofuel. Therefore, a macroalgae feedstock to be used for biofuel and biorefinery purpose should consists of the desired characteristics such as easy vegetative propagation, simple life or reproductive cycle, high growth rate and carbohydrate content, pest resistant, withstanding high tides and currents, high calorific value, low moisture, ash, nitrogen and sulphur content (Milledge and Harvey, 2016). Based on the above characteristics, macroalgae such as

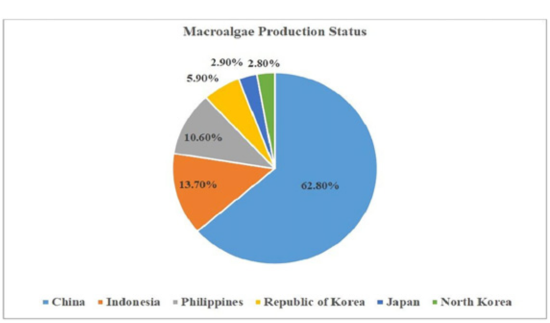

Fig. 1. Major macroalgae producing countries. Source: Food and Agriculture Organization (2016).

Gelidium pusillum, *Ulva fasciata*, *Sargassum latifolium*, *Ulva latuca*, *Gelidium elegans*, etc. were largely exploited from the past five years for the production of bioethanol and other valuable products (Baghel et al., 2015; Trivedi et al., 2016; Soliman et al., 2018; İnan and Özçimen, 2019; Hessami et al., 2019).

4.1. Summary

In this section, global seaweed and macroalgae production status has been detailed. Though the production status of macroalgae is quite good, suitable strain selection is indeed necessary for multi-products generation. The strain should have the characteristics of high growth rate, high carbohydrate content, and withstand the seasonal variations.

5. Macroalgal biomass cultivation and harvesting

For implementation of large scale sustainable biorefineries, macroalgal biomass cultivation cannot rely on onshore or near shore practices and on harvesting of wild type varieties. Onshore and near shore farming practices usually compete for edible food production such as fish production through aquaculture and utilization of coastal areas, whereas harvesting of wild type macroalgae varieties led to over exploitation of particular species (Buschmann et al., 2017; Alemañ et al., 2019). In order to overcome from the limitations of such farming practices, Azevedo et al. (2019) carried out cultivation of macroalgae (*Saccharina latissima*) under exposed offshore conditions for biofuels and feed production. Offshore macroalgal biomass production for biofuels also includes an important aspect of species selection. Before selection of appropriate macroalgae species and cultivation site, different physicochemical and biological factors have to be examined. Moreover, the proposed application should be well defined and clear in advance (Fernand et al., 2017a, 2017b). For example, various type of macroalgae could be selected for their utilization in low cost fuel production process along with their applications in high value compounds extraction and other value added products generation. Important physicochemical and biological factors include light, nutrients, temperature, wave velocity and the capacity to withstand extreme currents and high waves in offshore waters. Seaweed growth is most often affected in the presence of nitrogen, but phosphorous may also act as limiting factor in some systems (Rabalais, 2002).

In addition, knowledge related to the life cycle of various macroalgal species facilitate a proper design of cultivation cycle. Thus, cultivation system of macroalgae may consist of several steps such as exposed open sea system and ponds or on-land tanks (Santelices, 1999; Buschmann et al., 2017). Moreover, a nursery or hatchery cultivation might be used prior to open large scale cultivation of macroalgae which helps in continuous cultivation and avoids the chances of seasonal variations and susceptibility of diseases, pests, and biomass degradation (Gupta et al., 2018). Traditional offshore macroalgal cultivation systems consist of low cost materials such as lines, nets, ropes, cages, and rafts with minimum maintenance cost (Fernand et al., 2017a, 2017b). Advanced macroalgae cultivation systems include offshore ring for green macroalgae production, an easily operated base for cultivation of rope, and the attached, multi-body macroalgae farm designed to resist the harsh offshore conditions (Buck and Buchholz, 2005; Olanrewaju et al., 2017). Lehahn et al. (2016) examined the prospects of offshore macroalgae (*Ulva*) based biorefineries to provide energy, food, and chemicals. This analysis also investigated in depth regarding cultivation areas, limitations, benefits and environmental risks of large scale offshore cultivation of macroalgae. Another approach for macroalgae cultivation is through indoor seedlings transplantation followed by culture under greenhouse condition. Thereafter, developed fronds were transplanted onto ropes imbibed in the sea (Peteiro et al., 2014). Feedstocks of certain macroalgae are already produced under controlled laboratory conditions (Choi et al., 2002; Wichard, 2015). Availability of macroalgal biomass during rainy and winter seasons is usually not enough due to seasonal variations. Thus, co-cultivation of different macroalgae species can enhance the biomass productivity by increasing efficiency of light harvesting. This can be carried out by layered macroalgae cultivation system employing the light absorption properties of red, brown, and green macroalgae, thus enhancing light use (Reith et al., 2005; Fernández et al., 2019).

Biofuels and bioproducts generation from macroalgae will only be economically feasible if the harvesting cost of the macroalgal biomass are low (Horn, 2000). As benthic inhabitant, macroalgae are normally attached to the rough hard surface but some species have the ability to float in the seawater surface (Dębowski et al., 2013). Depending on the types of macroalgae species, harvesting is usually carried out at shallow water or from subtidal zone. Several techniques such as simple hand picking, cutting macroalgae thalli, boat, bulldoze, or tractor harvesting were used to harvest the macroalgae (Kirkman and Kendrick, 1997). Skimmer boats were employed to harvest the macroalgae far from the sea coast such as for *Laminaria digitata* (Fernand et al., 2017a, 2017b). However, harvesting naturally may pose some threat to environment unless the harvesting cycle of a particular macroalgae species is followed to permit recovery (Christie et al., 1998; Werner and Kraan, 2004).

5.1. Summary

Sustainable production of macroalgal biomass depends on cost effective cultivation and harvesting practices. Onshore and near shore macroalgae farming practices usually capture the coastal areas engaged in fish production, thus offshore farming practices normally recommended for macroalgae cultivation. Offshore cultivation is further considered as economical due to ease in installation and low cost maintenance. Apart from offshore cultivation, co-cultivation of different macroalgae species also enhanced biomass production due to increase in light harvesting efficiency. Biomass harvesting depends on whether macroalgae are free floating or attached to the surface. Hand picking, cutting, skimmer boats, bulldoze, and tractor harvesting were normally used to harvest macroalgae in an economical way.

6. Occurrence of different structural polysaccharides in macroalgae

Macroscopic seaweeds are normally referred as macroalgae having defined structures and specialized multicellular tissues similar to the plant roots and leaves (John and Anisha, 2011; Murphy et al., 2013). Moreover, compared to microalgae, macroalgae are less versatile and are categorized into three different forms based on the types of pigment present, i.e. brown (fucoxanthin and chlorophyll *c*), red (chlorophyll *a* and pycobilin) and green (chlorophyll *a* and chlorophyll *b*), respectively (Jung et al., 2013). Macroalgae has added benefit of higher photosynthetic rate compared to terrestrial plants and as a result they grow faster and produce large quantity of biomass per unit area (Murphy et al., 2013; Yanagisawa et al., 2013). The cell wall of macroalgae consists of outer covering of mucilaginous matrix containing amorphous sulfated galactan polymers such as agar, carrageenans and alginates, whereas the inner rigid layer is composed of cellulose microfibrils (Arad and Levy-Ontman, 2010). Macroalgae contains high levels of various structural polysaccharides of industrial importance that also acts as energy dense precursors for liquid biofuels production (Table 2).

The major cell wall polysaccharide of algae is cellulose and it is prevalent in most of the algal groups. Moreover, macroalgae also builds up other structural polysaccharides into the cell wall in significant quantity which can be further transformed into liquid biofuels. These polysaccharides are of macroalgal group specific, such as alginate particularly present in brown macroalgae, while agarose and carrageenan usually occur in red macroalgae. In case of green macroalgae, carbohydrate signatures typical to higher plants of low cellulose content were present (Vreeland and Kloareg, 2000; Murphy et al., 2013). Red and brown macroalgae contains sufficient quantity of unique carbohydrates but their direct transformation to biochemicals is not as simple through the developed conversion technologies of higher plants or lignocellulose. In addition, macroalgae are believed to possess low lignin or no lignin at all (Yanagisawa et al., 2011).

Compounds such as agar, carrageenan, and alginate have commercial importance and have potential market value in the present scenario. These compounds are group specific and some of them such as alginates and agarose are recalcitrant to fermentation and needs even more improved conversion technologies in future (Forro, 1987). In macroalgae, lipids constitute typically less than 5% of total dry biomass that are too low for biodiesel production (McDermid and Stuercke, 2003). Due to low lipid content, biofuels production from macroalgae is heavily dependent upon the conversion of carbohydrates rather than energy-rich oils extraction that can be further processed to an array of hydrocarbons or biodiesel (İnan and Özçimen, 2019).

6.1. Summary

The economic potential and production efficiency of a biorefinery to produce biofuels and bioproducts heavily depend on macroalgal biomass composition. Thus, a complete understanding on macroalgae composition is required to develop a macroalgae based biorefinery process (Song et al., 2015). The major polysaccharide found in the cell wall of most of the macroalgae is cellulose. Apart from this, polysaccharides such as agar, carrageenan, alginate, laminarin, mannitol, starch, ulvan, etc. were observed in several species of macroalgae. Since the

Table 2
Occurrence of different types of polysaccharides in macroalgae.

Compound	Monomer Units	Glycosidic Bonds Involved	Amount (%, dcw)	Occurrence	Biofuel Potential	Reference
Cellulose	D-Glucose	β-(1 → 4)	30–70 (red), 25–40 (green) and 30–50 (brown)	Red, brown and green algae	Glucose to ethanol	(Goh and Lee, 2010), (Jung et al., 2013), (Hou et al., 2015)
Agarose	Galactose and anhydro-L-galactose	β-(1 → 4) and α-(1 → 3)	10–52	Red algae	Galactose and anhydro-L-galactose to ethanol	(Lobban and Wynne, 1981)
Carrageenan	Galactose and anhydro-D-galactose	β-(1 → 4) and α-(1 → 3)	5–75	Red algae	Galactose and anhydro-D-galactose to glucose	(Lobban and Wynne, 1981)
Alginate	α-Guluronate and β-d-mannuronate	β-(1 → 4) and α-(1 → 4)	40	Brown algae	Nil	(Chen et al., 2015)
Fucoidin	L-fucose	α-(1 → 2)	5–20	Brown algae	Nil	(Al Abdallah et al., 2016)
Ulvan	Glucuronic acid, xylose, Sulfated rhamnose and iduronic acid	β-(1 → 4) and α-(1 → 4)	8–29	Green algae	Nil	(Al Abdallah et al., 2016)

composition of polysaccharides varies among different species of macroalgae, it is essential to ascertain their individual compositions to produce bioethanol and other value added products efficiently.

7. Macroalgae: a viable biomass feedstock for biofuels and biocommodities

Macroalgae are considered as a potential biomass feedstock for the production of biofuels and biocommodities due to their high photosynthetic rate and production of more biomass per unit area (Murphy et al., 2013; Yanagisawa et al., 2013). Though lignocellulose biomass holds a good potential for bioenergy generation, it consists of four major process steps in biofuel production technology (Fig. 2). Thus, it would add certainly more cost to the total production process. Each individual step contributes a certain cost to the total production process. Firstly, the major hurdle in biofuel (especially ethanol/butanol) production from lignocellulosics is the degradation or removal of recalcitrant lignin which is composed of phenylpropane units linked by alkyl-alkyl, aryl-aryl, alkyl-aryl linkages to access the cellulose and hemicellulose. Lignin is highly resistant to degradation and also a key inhibitor for conversion of cellulose and hemicellulose to fermentable sugars (Kumar and Sharma, 2017). Lignocellulosic biomass roughly contain 15–30% (*w*/w) lignin (Saha and Cotta, 2008) that contributes additional cost for delignification and also the treatment and disposal of black liquor (pretreated liquid) makes it a tedious procedure that augment to the entire cost of production, thereby making it a cost intensive process. Whereas, macroalgae does not contain lignin therefore it is easy to process without much of additional steps for its utilization. Secondly, the lignocellulosic biomass requires land for its growth if the biomass is a bioenergy group. In case of macroalgae, it can be grown in wastewater also with simultaneous advantage of biomass growth and waste treatment. Thirdly, apart from the biofuel production, a lot of value added chemicals such as pigments, vitamins, proteins can be extracted from macroalgae that could serve as a biorefinery option in which economy from the source is relatively higher. In lignocellulosic biomass, however, either gasification or valorization of final residue as fertilizer could be the only option.

The macroalgal biomass based biofuel technology that requires less process steps might emerge as low cost biofuel technology (Fig. 2.). The macroalgal biomass due to absence or low lignin content generally does not require the biomass pretreatment step for lignin degradation and thus cost effective in nature (Konda et al., 2015). In order to deconstruct the macroalgal cell wall (dried biomass) and to release the organic matter for either microorganisms, enzymes or chemicals to act on, an initial biomass processing/pretreatment methods such as maceration, milling, thermal or extrusion are necessary (Chen et al., 2015). Apart from biofuel production, a broad range of products can be produced such as proteins (lectin and taurine), fibers (ulvan), vitamins (tocols), and antioxidants (carotenoids, chlorophylls, bromophenol, phloroglucinol) with high nutritional properties (Zollmann et al., 2019).

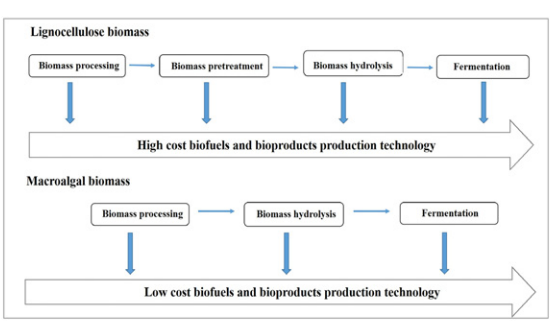

Fig. 2. Schematic diagram of lignocellulosic and macroalgal biomass production technology.

The marine biomass, specifically marine macroalgae from the last decade has given importance for only human consumption but nowadays gaining attention for its utilization in renewable fuels production. However, from the economic point of view, macroalgal biofuels necessitate the co-production of value added products of proven market value from algal biomass. Thus, a sustainable and viable biorefinery technology is indispensable that exploits maximally a feedstock for the production of fuel and an array of by-products. Konda et al. (2015) performed a comprehensive techno-economic analysis on macroalgae (*Saccharina latissima*) to ethanol biorefinery without pretreatment (for lignin removal) which would otherwise normally be observed in lignocellulosic biorefinery. According to the analysis, macroalgae may provide an economically viable podium for the generation of value added industrial products under suitable market conditions. This further supports the co-production approach for the successful biorefinery establishment.

From the last decade, the production processes exploiting macroalgae were specifically focused on the generation of single products, while the leftover solid or liquid waste remains unutilized (Zollmann et al., 2019). Moreover, most of the seaweed research ventures predominantly focused on biofuels production only (Murphy et al., 2013; van Hal et al., 2014; Baghel et al., 2015; Jiang et al., 2016a; Gegg and Wells, 2017). Recently, co-production or cascading strategy were employed to produce two or a series of products apart from the main targeted product, thus maximizing full utilization of the biomass (Gajaria et al., 2017; Nunes et al., 2018; Ingle et al., 2018; Peñuela et al., 2018; Hessami et al., 2019; Mhatre et al., 2019; Sadhukhan et al., 2019). Some of the macroalgae based complete biorefinery approach has been suggested to produce various products at different process steps. For example, the proposed cascading processes provide a complete utilization of macroalgal biomass (*Ulva lactuca*, *Gracilaria corticata*, and *Kappaphycus alvarezii*), solvents recycling leaving no residue unutilized, and recovery of products, namely protein, ulvan, mineral-rich liquid, methane, phycoerythrin, phycocyanin, lipid, agar, biofertilizer, and bioethanol (Mhatre et al., 2019; Ingle et al., 2018; Baghel et al., 2015).

The present review describes a holistic production process for the complete utilization of macroalgal biomass for variety of industrially valuable products such as lipids, pigments, fertilizer, agar, biomanure along with fuel ethanol. Furthermore, no waste is generated in this process as the residual biomass after fermentation can be used for biomanure, biogas, bio-oil, syngas, and biochar production. The produced biomanure later can be applied to improve the soil quality. The wastewater generated after each production process further can be utilized for growth and cultivation of macroalgal biomass. Thus, a zero waste technology can be possible through the biorefining of macroalgal biomass (Fig. 3). Moreover, the by-products obtained from the extended bioethanol production process in the long term may jeopardize the multibillion hydrocolloid seaweed industry (Bixler and Porse, 2011).

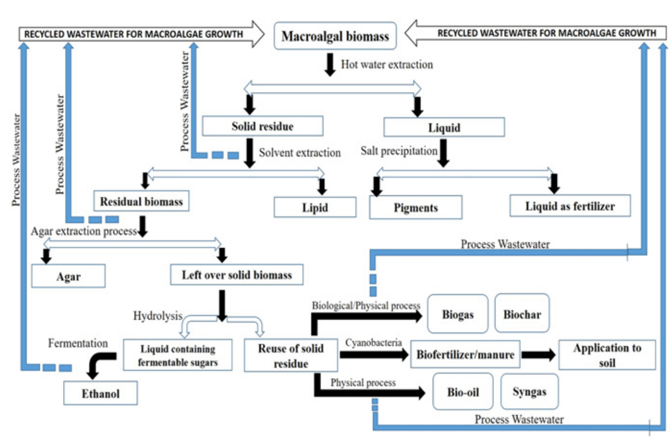

Fig. 3. Macroalgae based zero waste technology process.

Macroalgae cultivation and its utilization in biofuel conversion process results in large amount of liquid waste. Processing of liquid waste and its recycling is indeed necessary to reduce the water footprint and sustainable production of energy. However, liquid waste handling methods such as filtration, flocculation, and centrifugation play an important role in effluent property and its subsequent conversion process. Thus, macroalgal strain having the property of auto sedimentation can considerably minimize the use of chemicals during liquid waste handling and accordingly increase the reusability prospects (Mishra et al., 2019). Auto sedimentation allows the high density biomass to settle overnight and facilitates the removal of cells or debris prior to recycling of the liquid medium.

Macroalgae possesses the characteristics of high rate of biomass production and carbon fixation (Cole et al., 2014). Furthermore, macroalgae can be cultured using industrial, municipal, and agricultural wastewater (Roberts et al., 2015a; Cole et al., 2015; Neveux et al., 2016). Thus, wastewater harvested after each process steps can be recycled for macroalgal growth. Cole et al. (2016) carried out an extensive study on water recycling after hydrothermal liquefaction of green macroalgae *Oedogonium* and its further application on algal growth and recovery of water soluble chemicals. Also, carbohydrates produced by macroalgae act as an additional source of carbon, thus supports the macroalgae growth in recycled medium (Kim et al., 2014). Sometimes, low growth rate of macroalgae was observed due to inhibitory substances, high salt concentration, and reduced concentration of nutrient in the recycled water (Mishra et al., 2019). Thus, effects of harvested recycled medium must be examined carefully for making macroalgae based zero waste biorefinery a clean technology.

7.1. Summary

Macroalgae is considered as a promising candidate to remove the vulnerability of energy sector because of less number of products formation steps and low cost downstream processing. Earlier, macroalgae was utilized either for food or fuel production and thus macroalgal research has been concentrated only for single product formation. Nowadays due to its wide spectrum of polysaccharides content and developed conversion technologies, full biomass potential was realized. Macroalgae based co-production or cascading biorefinery approaches on zero waste concept were gaining attention for the production of both fuels and other industrially valuable products and to make the process even more feasible and cost-effective.

8. Limitations of the existing biofuel production processes

The second generation biomass is generally termed as lignocellulosic biomass which is indeed non-edible like algal biomass sources. Lignocellulosic biomass mainly consists of cellulose (40–60%, w/w), hemicellulose (20–30%, w/w) and lignin (15–30%, w/w) (Saha and Cotta, 2008) (Fig. 4). Cellulose and hemicellulose are the major precursors for biofuels and bioproducts formation. Lignin is a complex and recalcitrant polyphenolic compound that forms envelope around cellulose and hemicellulose. Consequently, accessibility of hydrolytic enzymes towards cellulose and hemicellulose has been hampered due to the presence of lignin and in turn slow down the process of biofuels production (Martín-Sampedro et al., 2013; Pareek et al., 2013; Rahikainen et al., 2013).

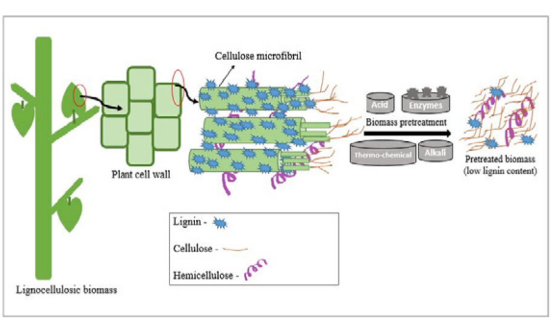

Fig. 4. Scheme on lignocellulose structure and biomass pretreatment.

A multitude of different biomass pretreatment techniques for lignin degradation have been developed in the last few decades that includes physical, chemical, physico-chemical, and biological means (Baruah et al., 2018). Physical pretreatment methods (milling, microwave irradiation, extrusion, and ultrasonication) of lignocellulosic biomass are ecofriendly and do not generate any toxic material. However, it suffers from the limitation of high energy consumption (Shirkavand et al., 2016). Chemical methods include both alkali and acid mediated biomass pretreatment. Alkali pretreatment is based on the lignin solubilization in the alkali solution due to cleavage of the ester linkages between lignin and hemicelluloses. Application of calcium hydroxide or lime for biomass pretreatment is found to be simple and effective as calcium hydroxide is inexpensive and easy to handle. The major disadvantage of the alkali pretreatment is the recovery of the added alkali from the reaction mixture that further requires investigation (Sun et al., 2016). Acid pretreatment of lignocellulosic biomass is dependent on the susceptibility of the glycosidic bonds present between cellulose and hemicellulose towards acid. It can be performed by using either dilute acids (0.1–10% (v/w)) at high temperature or concentrated acids (30–70% (v/w) at low temperature. Acid pretreatment methods preferably result in good sugar conversion yield compared to other pretreatment modes while at the same time generates inhibitory byproducts and are corrosive in nature. Moreover, pretreated biomass neutralization is required which adds further negative effect to the downstream processes (Baruah et al., 2018). Physico-chemical biomass pretreatment is the most effective and extensively employed pretreatment method that includes a combination of mechanical forces and chemical effects. The method has several advantages such as limited chemical use, high sugar recovery, low recycling costs, high energy efficiency, and low environmental effect (Pielhop et al., 2016). However, harsh reaction conditions led to the generation of inhibitors (Lizasoain et al., 2017) such as weak acids and furan derivatives that affect the subsequent hydrolysis process (Sun et al., 2015; Verardi et al., 2018).

Biological and enzymatic mode of lignin degradation are the promising approaches in the process of lignocellulosic biofuels production as it does not hamper the enzymes or organisms involved in later steps (Shruti and Malik, 2015; Rajak and Banerjee, 2018; Ahmed et al., 2018). However, isolation of microbes and enzyme production for lignin removal or degradation would further increase the cost of the biofuels production process. In addition, for lignocellulosic derived fuels to have a significant influence on energy demand, there should be a consistent large scale availability of suitable feedstock along with an energetically favorable conversion processes to valorize this biomass feedstock into a useable fuel (Cole et al., 2016). However, the feasibility of second generation biofuels production in terms of its commercialization is only restricted to the countries having huge forestry and agricultural lands. In this respect, macroalgae is considered to be an untapped resource which can be employed for the production of biofuels and other biocommodities.

8.1. Summary

Biofuels and bioproducts generation by utilizing lignocellulosic biomass is a well-developed technique. However, this established second generation feedstock based production process has only limited success because of the presence of recalcitrant compounds such as lignin that make the lignocellulosic biomass resistant to biological and chemical conversions (De Bhowmick et al., 2019). Thus, macroalgae acts as a suitable feedstock for bioconversion process due to the absence of recalcitrant or complicated compounds.

9. Macroalgal biomass hydrolysis for fermentable sugars production

The key step for any biofuels and bioproducts generation process is to first establish a cost effective pretreatment methodology. However, pretreatment is not required in the case of macroalgae due to little or no lignin content (Sadhukhan et al., 2019). Thus, the major focus lies on the biomass hydrolysis, i.e. to deconstruct the algal polysaccharides to sugar monomers or other valuable compounds. Nowadays, chemical, physical and biological modes of hydrolysis have been studied by exploiting a wide range of macroalgal species for energy and other by-products generation but are in their early phase of development (Jiang et al., 2016). Dilute acid, hydrothermal and thermochemical were conventional hydrolysis methods. All of these methods either result in the formation of toxins or inhibitors which are not favored during fermentation and thus reduced yield of the final product was observed (Jiang et al., 2016). Also, it is very difficult to control the process parameters during acid or alkali hydrolysis. Different types of biomass hydrolysis methodologies by utilizing macroalgae as feedstock were explained in detail with process optimal conditions (Table 2). Hydrolysis is usually carried out to deconstruct polymeric chains of different polysaccharides into monomeric sugars and can be operated as a single step followed by fermentation or done simultaneously with fermentation. The mode of hydrolysis is normally acid or through thermochemical, but in the recent years enzymes have been preferred over acid (Hebbale et al., 2019; Saravanan et al., 2018; Trivedi et al., 2016; Tan and Lee, 2016; Nguyen et al., 2016). Hessami et al. (2019) reported sugars yield of 0.44 g/g from *Gelidium elegans* as a macroalgal feedstock after dilute acid hydrolysis under the optimized conditions at 2.5% (w/v) H_2SO_4, 120 °C for 40 min. The major limitation behind the use of acid is its non-selective nature of action. Consequently, it hydrolyzes all of the biomass components and produces fermentation inhibitors at harsh operating conditions (Jiang et al., 2016). Furthermore, acid hydrolysate is later required to be neutralized for being used in fermentation.

Enzymatic hydrolysis overcomes the shortcomings observed during acid hydrolysis because enzymes have their own selectivity towards specific linkages and thus minimizes the formation of unnecessary products (Jang et al., 2012). Moreover, the approach of enzymatic venture for sugars generation from macroalgae or cellulosic biomass is more effective in terms of high conversion yield (Trivedi et al., 2016; Tan and Lee, 2016; Baghel et al., 2015). Trivedi et al. (2016) and Baghel et al. (2015) carried out an in depth study on macroalgal biomass (*Ulva fasciata* and *Gelidium pusillum*) hydrolysis where crude cellulase preparations were used to produce high concentration of fermentable sugars. However, macroalgae are comprised of diversified types of polysaccharides which required tailor made enzyme cocktails to degrade but till now no such enzymatic cocktail is available or reported as robust degraders (Choi et al., 2009). Most of the works reported in Table 3 have employed produced cellulase or commercial cellulase preparations that contain multiple enzyme such as cellulase and xylanase (Hebbale et al., 2019; Saravanan et al., 2018; Tan and Lee, 2016; Nguyen et al., 2016; Trivedi et al., 2016). Moreover, understanding of the mechanism of enzyme actions is important as well because this will facilitate the proper design of energy efficient biorefineries.

9.1. Summary

Biomass hydrolysis is one of the important steps in macroalgae based biofuels and products generation technology. The method of biomass hydrolysis to fermentable sugars is normally carried out through acid or thermochemical means. These modes of hydrolysis have limitations such as formation of toxins and fermentation inhibitors. Thus, enzymes were preferred over these methods. Enzymes or cocktail of enzymes have specific properties and act on particular compound without altering the structure of other compounds and therefore increase the yield of the product while minimize the formation of unnecessary products.

10. Fermentation

The composition of biomass feedstock plays a vital role in determining the types of bioprocess to be used for energy generation. In general, macroalgae is first subjected to initial processing which includes dewatering and size reduction followed by hydrolysis of the biomass to form simple sugars and finally fermentation of the simple sugars to ethanol. Based on which combination of process steps to occur, the processes are categorized into (i) separate hydrolysis and fermentation (SHF), where hydrolysis and fermentation of the processed biomass are carried out in two different vessels with different reaction conditions, (ii) simultaneous saccharification and fermentation (SSF), in which both hydrolysis and fermentation of the processed biomass are carried out in a single unit with same reaction conditions, and (iii) consolidated biomass processing (CBP), where enzyme production, biomass hydrolysis and fermentation are performed in a single reactor with the same reaction environment. Fermentation of the macroalgal feedstock is mainly carried out by two processes, SHF and SSF (Taherzadeh and Karimi, 2007; Gírio et al., 2010).

The most widely used process is SSF from the last decade and also the major technology in the case of lignocellulosic biofuel production (Kim et al., 2011; Lee et al., 2013; Tan and Lee, 2014). The simultaneous process is highly compatible because the enzymes and microbes work optimally under the similar process conditions. The main advantage of the SSF is that the released sugars from different polysaccharides can be effectively utilized for biofuels production instead of being accumulated during the reaction. Nevertheless, in the case of macroalgae, both SHF and SSF reported quite good and encouraging results in ethanol production which substantiates the feasibility of the biomass type towards its valorization (Table 3). İnan and Özçimen (2019) carried out SHF of acid (2 N sulfuric acid) pretreated macroalgal biomass *Ulva lactuca* under optimum process conditions and recorded bioethanol yield of 24.48% within 60 min of incubation time. Similarly, Saravanan et al. (2018) performed SHF of two stage (acid and enzyme) hydrolyzed *Gracilaria* biomass and reported an improved ethanol yield of 28.7 g/L. In another study, Trivedi et al. (2016) described an integrated sequential products generation process where ethanol was produced from extracted cellulose after ulvan extraction using *Ulva fasciata* as a feedstock. The yield of ethanol (29.58 g/L) was high because the extracted cellulose was enriched with peptone and yeast extract. Tan and Lee (2016) studied SSF of solid acid hydrolyzed *Eucheuma cottonii* hydrolysate and reported 11.60 g/L of ethanol. However, it should be noted that use of different fermentative microorganisms during SSF may inhibit the hydrolytic enzyme activity and thus could decrease the fuel yield (Reddy et al., 2008; Holtkamp et al., 2009). Also, the high degree of complexity of macroalgal polysaccharides leads to low biofuel yield due to its non-utilization by the fermenting microbes (Jang et al., 2012). Recently, with the advancement in biotechnology and cutting edge tools, genetic and metabolic engineering approaches have gained importance towards its application in macroalgal biorefinery. The above mentioned challenges can be resolved through biorefinery based on CBP which have the capability to generate a variety of products from various precursors. CBP is usually performed with the genetically or metabolically modified microorganisms having multiple functionalities and is expected to impart a breakthrough in the development of macroalgal based energy and products generation in the coming years. For example, bioethanol was derived from alginate by inserting alginate lyases from *Vibrio splendidus* into the *Escherichia coli* genome. This engineering approach has reported 4.7% (v/v) of ethanol which is regarded as ideal for macroalgae (Wargacki et al., 2012). Apart from the aforementioned fermentation methods, simultaneous saccharification and co-fermentation (SSCF) is another mode which involves specifically fermentation of one or more substrates with single or more inoculum in a common platform. The SSCF process includes the simultaneous fermentation of mixed sugars such as the fermentation of galactose and glucose rich liquid fractions that resulted in ethanol yield of 64.3 g/L

Table 3
Biomass hydrolysis methods with respect to the different macroalgae species.

Macroalgae	Treatment	Temperature	Reaction Time	Optimal Conditions	Total sugars (g/g)	References
Ulva intestinalis and *Ulva lactuca*	Cellulase	55 °C	36 h	Biomass: 5% (w/v) with respect to enzyme Hydrolysis at 55 °C, pH 6.8 for 36 h, sugars estimated at every 6 h	0.13 and 0.10	(Hebbale et al., 2019)
Gelidium elegans	Dilute acid	120 °C	40 min	Biomass: 5% (w/v) Hydrolysis at 2.5% (w/v) H_2SO_4 at 120 °C for 40 min	0.44	(Hessami et al., 2019)
Sargassum latifolium	Sequential treatment through thermochemical and with *Trichoderma asperellum* RM1	100 and 120 °C (hydrothermal) and 30 °C (fungal)	30 and 60 min (Thermochemical), 21 days (fungal)	Biomass: 10% (w/v) (thermochemical), 10% (w/v) (fungal) Hydrolysis at 120 °C and 60 min with 3% H_2SO_4 and 1% HCl, 100 °C and 60 min with 0.5% NaOH (Thermochemical) Hydrolysis at 30 °C under static conditions for 21 days (fungal)	0.51	(Soliman et al., 2018)
Gracilaria sp.	Sequential dilute acid and cellulase	121 °C (acid) and 50 °C (enzyme)	30 min (acid) 4 h (enzyme)	Biomass: 2.5% (w/v) with respect to liquid Hydrolysis at 121 °C for 30 min followed by incubation for 1 h at 30 °C under shaking condition Enzymatic hydrolysis of acid hydrolysate at 50 °C, pH 5.0 and 150 rpm for 4 h	0.14	(Saravanan et al., 2018)
Gelidium amansii	Dicationic acidic ionic liquids	120°C	3 min	Biomass: 5% (w/v) Hydrolysis with 0.5 mmol of ionic liquid [Tri-EG-$(MIm)_2$] $2HSO_4$ at 120°C for 3 min	0.33	(Malihan et al., 2017)
Ulva fasciata	Cellulase	45°C	6 h	Biomass: 2% (w/v) with respect to enzyme Hydrolysis at 45°C for 36h	0.94	(Trivedi et al., 2016)
Eucheuma cottonii	Sequential treatment with solid acid and cellulase	120 °C (solid acid hydrolysis) and 50 °C (enzymatic)	1 h (solid acid hydrolysis) and 30 h (enzymatic)	Biomass: 16 wt% Hydrolysis with Dowex (TM) Dr-G8 at 120 °C for 1 h (solid acid) Biomass: 2% with respect to enzyme Hydrolysis with cellulase at 50 °C, pH 4.8 for 30 h (enzymatic)	0.61	(Tan and Lee, 2016)
Ulva sp.	Thermochemical	121 °C	30 min	Biomass: 15% (w/v) Hydrolysis with 2% H_2SO_4 at 121°C for 30 min	0.22	(Jiang et al., 2016)
Kappaphycus alvarezii	Celluclast 1.5 L	45 °C	48 h	Biomass: 12% (w/v) with respect to enzyme Hydrolysis at 45 °C for 48 h	0.19	(Nguyen et al., 2016)
Gelidium amansii	Autoclave	121 °C	1 h	Biomass: 2.5% (w/v) with respect to water Hydrolysis at 121 °C for 1 h	0.22	(Kim et al., 2015)
Ulva fasciata	Cellulase	40 °C	24 h	Biomass: 4% (w/v) with respect to enzyme Hydrolysis at 40 °C and pH 4 for incubation time of 24 h	0.11	(Trivedi et al., 2015)
Gelidium pusillum	Cellulase	45 °C	48 h	Biomass: 1.6% (w/v) with respect to enzyme Hydrolysis at 45 °C and pH 4.8 for 48 h under shaking condition	0.93	(Baghel et al., 2015)

upon using *Kappaphycus alvarezii* as a macroalgal feedstock (Neves et al., 2007; Hargreaves et al., 2013).

Fermentation of the released simple sugars from macroalgae is mainly done by the yeast *Saccharomyces cerevisiae*, which is by far the most exploited species for ethanol production industrially (İnan and Özçimen, 2019; Hessami et al., 2019; Saravanan et al., 2018) The major limitations of *S. cerevisiae* is that it cannot ferment pentose sugars and thus necessitates the requirement of pentose fermenting yeast strains such as *Pichia stipites* and *Kluyveromyces marxianus* (Obata et al., 2016). The examples of detailed macroalgal biomass processing in the laboratory scale for bioethanol production are described in Table 4.

The process of macroalgae based bioethanol production would be economically feasible only when the production digits or concentrations of ethanol were higher than 4% (40 g/L) (Yanagisawa et al., 2013). Brockmann et al. (2015) performed a life cycle assessment on bioethanol production from onshore cultivated green macroalgae (*Ulva* sp.) and proposed that macroalgal derived bioethanol is as efficient as fossil fuel and sugarcane based bioethanol. Moreover, apart from the bioethanol, macroalgal biomass has the potential to produce

Table 4
Bioethanol production from macroalgal biomass by different fermentation methods.

Macroalgae	Yeast	Mode of fermentation	Optimum Conditions	Ethanol (%, g/L)	References
Ulva lactuca	*Saccharomyces cerevisiae*	Separate hydrolysis and fermentation (SHF)	Yeast volume: 3% (v/v) Reaction conditions: 40 °C, 150 rpm for 48 h	Yield: 24.48%	(İnan and Özçimen, 2019)
Gelidium elegans	*S. cerevisae*	SHF	Yeast volume: 5% (v/v) Reaction conditions: 30 °C under shaking condition for 48 h	13.27 g/L	(Hessami et al., 2019)
Gracilaria sp.	*S. cerevisiae*	SHF	Yeast volume: 2% (v/v) Reaction conditions: 30 °C, 125 rpm for 96 h	28.70 g/L	(Saravanan et al., 2018)
Sargassum latifolium	*S. cerevisiae* ATCC76621 and RM2	SHF	Yeast volume: 5% (v/v) Reaction conditions: 30 °C, 150 rpm for 48 h	3.17 g/L	(Soliman et al., 2018)
Padina tetrastromatica	*S. cerevisiae*	SHF in a desktop fermenter	Yeast volume: 3% (v/v) Reaction conditions: 30 °C under shaking condition for 144 h	21.17 g/L	(Ashokkumar et al., 2017)
Kappaphycus alvarezii	Galactose adapted yeasts, *S. cerevisiae* KCTC1126, *Kluyveromyces marxianus* KCTC7150, and *Candida lusitaniae* ATCC42720	SHF	Yeast volume: 2.5 g/L of yeast extract Reaction conditions: 30 °C, 150 rpm for 144 h	15.80 g/L	(Nguyen et al., 2016)
Chondrus crispus	*S. cerevisae*	SHF	Yeast volume: 10 g/L of yeast extract Reaction conditions: 30 °C, magnetic stirring at 120 rpm for 120 h	13.00 g/L	(Kostas et al., 2016)
Ulva fasciata	*S. cerevisiae* MTCC180	SHF	Yeast volume: 3 g/L of yeast extract Reaction conditions: 28 °C at 120 rpm for 12 h	29.58 g/L	(Trivedi et al., 2016)
Eucheuma cottonii	*S. cerevisae*	Simultaneous saccharificati-on and fermentation (SSF)	Biomass loading: 2% (w/v) with respect to enzyme Yeast volume: 1% (w/v) yeast extract Reaction conditions: 35 °C at 130 rpm for 96 h	11.60 g/L	(Tan and Lee, 2016)
Laminaria digitata	*Pichia stipitis* and *Kluyveromyces marxianus*	SHF	Yeast volume: 50 mL of seed culture of *P. stipitis and K. marxianus* Reaction conditions: 30 °C, 100 rpm for 150 h	5.8 g/L (*P. stipites*) and 6.0 g/L (*K. marxianus*)	(Obata et al., 2016)
Gelidium amansii	*S. cerevisiae* KCTC7906	SSF	Biomass loading: 15% (w/v), cellulase 8 mg/g, β-glucosidase 4 mg/g, dry yeast 100 mg Reaction conditions: 37 °C, 200 rpm for 48 h	3.78 g/L	(Kim et al., 2015)
Laminaria digitata	*S. cerevisae*	SHF and SSF	SHF Biomass loading: 20% (w/v) Yeast volume: 1% (w/v) Reaction conditions: 3 °C, 120 rpm for 48 h SSF Biomass loading: 10% (w/v), Celluclast 1.5 L (10%, v/w) and 0.25% (w/w) alginate lyase Reaction conditions: 2 h pre-hydrolysis step at 50 °C followed by fermentation at 32 °C, 150 rpm for 48 h	30.30 g/L (SHF) 14.70 g/L (SSF)	(Hou et al., 2015)

a superior quality of fuel called biobutanol through the acetone-butanol (AB) fermentation process. The AB fermentation is mainly carried out by anaerobic bacteria such as *Clostridium* sp. which is capable of generating a wide variety of compounds, namely butanol, acetone, and organic acids from different carbon sources. However, *Clostridium* sp. does not act on some of the glucose containing polysaccharides (mannitol obtained from brown algae) which resulted in low productivity of biofuels (Huesemann et al., 2012).

10.1. Summary

Macroalgal biomass fermentation is mainly performed through SHF and SSF. The results in terms of the production of ethanol and other products are encouraging. However, use of different types of fermentative microorganisms during SSF might further inhibit the activity of hydrolytic enzymes and thus could decrease yield of the final product. Hence, in future, CBP with genetically modified microorganisms is recommended because of multiple functionalities of the microorganisms that can be exploited to produce wide variety of products. Fermentation is usually carried out using *S. cerevisae* which cannot ferment pentose sugars. This limitation can be resolved by using pentose and hexose sugars fermenting strains together for ethanol production. Apart from ethanol, macroalgal biomass can also be used to produce even higher quality fuel such as butanol through AB fermentation process.

11. Beyond the flask: fermenter operations for macroalgal bioethanol production

Macroalgal biomass exploitation for third generation biofuels production has been received much attention due to high biomass yield, no lignin content and efficient carbon dioxide capture in coastal areas. However, still many refinements and development have to be needed to establish a cost effective technology for large scale macroalgal biomass processing. There are a few reports on large scale macroalgae processing for bioethanol production by utilizing genetically modified microorganisms. Gegg and Wells (2019) suggested that scaling up of macroalgal biomass with policy support can determine the viability of the seaweed derived fuels and products. Camus et al. (2016) reported the scale up studies for bioethanol production from macroalgae *Macrocystis pyrifera* by using a recombinant *E. coli* BAL1611 where the production process was scaled up from laboratory (1 L) to the 75 L bioreactor level. Fermentation at the laboratory scale showed that growth of biomass and yield were not much affected by changing the ratio of alginate and mannitol. The yield of ethanol was observed to be maximum when the alginate to mannitol ratio was maintained at around 5:8. In order to utilize most of the sugars during fermentation, a four stage process scaling up model was developed that includes acid leaching, deconstruction, hydrolysis, and fermentation. Using this process upon scaling up from 1 L to 75 L, a maximum of 8.87 g/L of ethanol was recorded after 48 h. In another study, Ra et al. (2014) described the scale up studies for bioethanol production from macroalgae *Undaria pinnatifida* where two stage biomass hydrolysis followed by fermentation through *Saccharomyces cerevisiae* KCCM 1129 was carried out and the process was scaled up from 5 L to 500 L level. According to this process, reduced ethanol yield was observed upon increasing the salinity above 80 psu (practical salinity unit). Thus, low slurry content (130 g dw/L) was selected as optimal value for ethanol production using 5 L fermenter. Fermentation by using 5 and 500 L fermenters showed ethanol yield of 8.5 g/L and 7.9 g/L and productivity of 0.44, and 0.41 g/L/h, respectively. The whole process description for the two macroalgae species along with ethanol concentration and productivity are given in Table 5. In addition, material and exergy flows during the conversion process play an important role and act as a major factor during biomass scaling up. Ingle et al. (2018) developed models to study the material and exergy flows in macroalgal biomass conversion process. The model examined the biorefining of macroalgae *Kappaphycus alvarezii* for the production of ethanol, fertilizer, carrageenan, and biogas. A computational model based on flux balance analysis was also developed to predict the different fermentation conditions and the most efficient conversion parameter of *K. alvarezii* to bioethanol.

11.1. Summary

Development in macroalgae based biofuels and bioproducts generation is restricted only to laboratory scale research. In order to analyze the feasibility of established processes, evaluation at large scale is indeed required. There are very few reports available in the scientific domain related to scaling up of macroalgal biomass for ethanol production. In addition, less number of reports on material and energy flow of the conversion processes are available. The available reports on scaling up detailed about the type of microorganisms used, biomass processing conditions, optimal hydrolysis and fermentation conditions, and concentration and yield of ethanol. Thus, in order to make the macroalgae based zero waste biorefinery process as a successful endeavor, more thrust should be given on biomass scaling up with techno economic analysis.

12. Value added products from fermented residual macroalgal biomass

The major limiting factor for macroalgal products commercialization is the production economics because laboratory and pilot scale research has dictated the high cost over profit ratio and is not under acceptable level (Nikolaisen et al., 2008). In this perspective, utilization of the residual/waste biomass under the principle of zero waste approach for value added products generation after biofuel production process may resolve the issue of production economics. The residual macroalgal biomass after biofuels generation, specifically ethanol, can be best possibly utilized for a range of high volume low value products formation. These by-products usually directed towards the value addition of the process and thus reduce the total production cost. Such type of synergistic approach makes the entire process economically feasible. The different types of by-products from the left over residual biomass after fuel production can be inferred from Fig. 5.

Biogas is produced from the organic matter present inside the macroalgal biomass which has the property of volatility and thus easily undergoes anaerobic fermentation to release gases like carbon dioxide, methane and hydrogen sulfide. Marine biomass has shown good potential for biomethane production and is around 140 mL and 280 mL of methane per gram of volatile solids for green and brown macroalgae (Charlier et al., 2007; Allen et al., 2013). Some studies have also reported high biomethane production of 260–500 mL per gram of volatile solids by using macroalgae such as *Gracilaria* sp., *Macrocystis* sp. and *Laminaria* sp. (Chynoweth, 2002; Singh and Gu, 2010; Parmar et al., 2011). Tabassum et al. (2018) performed a detailed study on biomethane production by utilizing different segments of seaweed thalli from various species of macroalgae. The highest yield of biomethane (286 L/kg of volatile solids) was obtained from the stipe segment of *Laminaria digitata*, whereas the lowest value of biomethane (118 L per kg of volatile solids) was recorded from the holdfast segment of *Laminaria hyperborean*. In addition, Pechsiri et al. (2016) has carried out a system analysis for biogas and fertilizer production using Kelp as macroalgae feedstock. In this study, they analyzed the production in terms of input energy and greenhouse gas emission performances to check the viability of the entire process.

Biofertilizer or manure is formed by the decomposition of organic matter which is normally carried out either by earthworm (vermicomposting) or through blue-green algae or macroalgae. Different types of macroalgae such as *Ascophyllum* sp., *Sargassum* sp., *Fucus* sp., *Laminaria* sp., *Ulva* sp., and *Gracilaria* sp. have the capability to enrich the low quality waste biomass with nutrients like nitrogen, phosphorous, and potassium (Nabti et al., 2017; Silva et al., 2019). The nitrogen

Table 5
Pilot scale study for bioethanol production from macroalgae.

Strain	Initial processing	Biomass hydrolysis	Fermentation	Ethanol concentration/productivity	References
1 L capacity					
M. pyrifera	(i) Milling of biomass to half inch pieces (ii) Bacterial inoculum preparation on M9 minimal media.	Three steps biomass hydrolysis were carried out namely, (i) Acid leaching with 0.3% hydrochloric acid Reaction conditions: 25 °C, 750 rpm, 1 h. (ii) Depolymerization of the residual leached macroalgal solid biomass with CTec2 (Cellulase complex), HTec2 (Endoxylanase), and alginate lyase. Reaction conditions: 50 °C, pH 5.5, 200 rpm, 20 h. (iii) Hydrolysis of depolymerized liquid with crude oligoalginate lyase lysate. Reaction conditions: 25 °C, pH 7.5, 500 rpm, 20 h.	Fermentations were carried out with the developed bacterial (*E. coli* BAL1611) inoculum (50 mL) in the 1 L reactors containing glucose (22.3 g/L), mannitol (44.6 g/L), and 4-deoxy-L-erythro-5-hexoseulose uronate (22.3 g/L) with the desired proportion of 1:2:1. Reaction conditions: 25 °C, 200 rpm, 141 h.	Concentration: 10.36 g/L after 41 h. Productivity: 0.25 g/L/h.	(Camus et al., 2016)
75 L capacity (same reaction conditions as mentioned for 1 L)					
M. pyrifera	(i) Milling of biomass to half inch pieces of around 100 kg. (ii) Bacterial inoculum was prepared overnight on M9 minimal media.	(i) 48 kg of leached residual solid biomass and 380 L of leachate were obtained after acid leaching. (ii) 210 L of depolymerized solution containing 2.6 g/L of glucose was obtained after treating the leached residual biomass with cellulase, endoxylanase and alginate lyase. (iii) Around 34.50 L of hydrolyzed liquid was obtained after treating the depolymerized liquid that contains 1.54 g/L of glucose and 22.3 g/L of 4-deoxy-L-erythro-5 hexoseulose urinate.	Fermentation was carried out with 7 L inoculum, 475 g of mannitol (22.3 L), 238 g of 4-deoxy-L-erythro-5 hexoseulose uronate (10.7 L) and 268 g of glucose in the tune of 40 L final volume with the desired proportion of 1:2:1.		
5 L capacity					
U. pinnatifida	(i) Hammer milling of dried macroalgae followed by powder separation with a 200-mesh sieve. (ii) Seed culture of *S. cerevisiae* KCCM 1129 was maintained on yeast peptone dextrose (YPD) media at 30 °C, 100 rpm, and 24 h incubation time.	(i) Thermal acid hydrolysis of *U. pinnatifida* (130 gdw/L slurry) was carried out with 75 mM H_2SO_4 Reaction conditions: 121 °C, 60 min. (ii) Thermal acid treated substrate then hydrolyzed with the commercial enzymes such as Celluclast 1.5 L (1%, v/v), Viscozyme L (1%, v/v), and Termamyl 120 L. Reaction conditions: Termamyl 120 L was used during thermal acid hydrolysis (121 °C, 60 min) Celluclast 1.5 L and Viscozyme L were used during enzymatic hydrolysis (45 °C, 150 rpm, 24 h).	The obtained hydrolysate (2.5 L) of *U. pinnatifida* after thermal and enzymatic hydrolysis was fermented under semi-anaerobic environment. Reaction conditions: 30 °C, 180 rpm, 72 h .	Concentration: 8.50 g/L after 24 h. Productivity: 0.35 g/L/h	(Ra et al., 2014)
500 L capacity (same reaction conditions as mentioned for 5 L)					
U. pinnatifida	(i) Hammer milling of dried macroalgae followed by powder separation with a 200-mesh sieve. (ii) Seed culture of *S. cerevisiae* KCCM 1129 was maintained on yeast peptone dextrose (YPD) media at 30 °C, 100 rpm, and 24 h incubation time.	(i) 35 kg of dry *U. pinnatifida* biomass with working volume of 300 L was subjected to thermal acid hydrolysis followed by enzymatic hydrolysis. (ii) The above hydrolysis methods result in the production of hydrolysates containing 3.5 kg of galactose and 2.5 kg of glucose.	Fermentations were carried out with the developed bacterial (*E. coli* BAL1611) inoculum (50 mL) in the 1 L reactors containing glucose (22.3 g/L), mannitol (44.6 g/L), and 4-deoxy-L-erythro-5-hexoseulose uronate (22.3 g/L) with the desired proportion of 1:2:1. Reaction conditions: 25 °C, 200 rpm, 141 h.	Concentration: 7.9 g/L after 18 h. Productivity: 0.43 g/L/h.	(Ra et al., 2014)

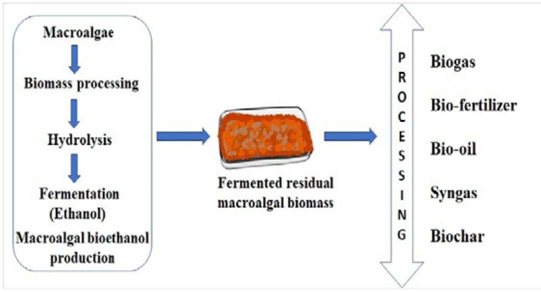

Fig. 5. Different types of by-products generation from fermented macroalgal biomass.

and phosphorous content in macroalgae primarily depends on their morphology rather than on environment (Bucholc et al., 2014). Kumar and Sahoo (2011) reported biofertilizer production from macroalgae *Sargassum wightii* that has positive effect on growth, germination and yield of *Triticum aestivum*. Similarly, Akila et al. (2019) utilized the residual solid biomass of *Ulva* sp. after biogas production for biofertilizer generation that increased phosphorus content (2.42 ± 0.5 mg/g). The obtained biofertilizer was then applied as soil conditioner to improve the soil quality.

The employment of non-edible or waste biomass for bio-oils production is becoming a popular trend for renewable energy generation. Bio-oil is usually leached out in the liquid phase when the algal biomass is subjected to high temperature in anaerobic conditions and based on the processing conditions and algal feedstocks, composition of the bio-oil varies accordingly (Iliopoulou et al., 2007; Yanqun et al., 2008). Different processes were adopted for bio-oil production by utilizing variety of macroalgal biomass. Hydrothermal liquefaction of *Sargassum* spp. resulted in bio-oil yield of $22.2 \pm 0.1\%$ (dry wt. basis), whereas 35 MJ/kg of bio-oil was reported after supercritical ethanol treatment by utilizing *Saccharina japonica* as a macroalgae feedstock (Díaz-Vázquez et al., 2015; Zeb et al., 2017).

Syngas is regarded as a potent fuel source because of its high energy density and can act as a raw feedstock for the production of specialty chemicals such as ethylene glycol and methanol. It is a mixture of different types of gases such as CO_2, CO, N_2, CH_4, and H_2 which can be generated through pyrolysis or gasification of biomass at high temperatures (700–1000 °C) or normal gasification by using oxygen and steam. Syngas is a low calorific gas and can be utilized directly to operate the gas turbines or used as a fuel as such (Behera et al., 2015). Microwave induced low temperature pyrolysis of red seaweed *Gracilaria gracilis* resulted in high syngas yield of 0.51 L per gram of pyrolysed material (Bermúdez et al., 2014). Similarly, Hong et al. (2017) reported syngas production (73.3%, v/v) through microwave assisted pyrolysis of macroalgal biomass of porphyra.

Macroalgae is considered as a viable biomass source which can be used for low value products generation such as nutrient-rich biochar. The decomposition of organic residues under limited oxygen conditions at 350 °C to 900 °C resulted in the formation of solid biochar that contains high amount of carbon. Apart from carbon, it is also composed of other elements, namely oxygen, sulphur, nitrogen, and hydrogen (Contreras-Porcia et al., 2018). Roberts et al. (2015) reported six macroalgae species that yielded biochar (45–62%) after slow pyrolysis at 450 °C for 1 h. Biochar has found many wide applications that include soil conditioner, pollutants adsorbent, greenhouse gas emissions reducer, and as a heat energy source. Macroalgae derived biochar has gained renewed interest because of high nutrient content (nitrogen and phosphorous) along with trace elements (calcium, magnesium, and potassium) that actually widen its application in various agricultural fields (Bird et al., 2012). In addition, Srinivasan et al. (2015) reported the use of biochar obtained from sewage and agricultural biomass as filler in biocomposites and wood. Furthermore, this gives a possibility of application of macroalgal biochar in the field of polymer biocomposites.

12.1. Summary

Most of the production processes involving macroalgae is concentrated mostly on single products. However, the production economics cannot be satisfied by the generation of single products. It needs co-production of other valuable products apart from the main targeted product. Due to diverse composition of different compounds in macroalgae compared to terrestrial plants, macroalgae based biorefinery process has a huge potential for the generation of biofuels and bioproducts (John and Anisha, 2011; Kraan, 2013). The fermented biomass after ethanol production can be utilized for the production of value added products such as biogas, biofertilizer, bio-oil, syngas, and biochar. These products due to their wide applications further add value addition to the production process.

13. Issues and barriers for macroalgal biofuels production

The high production status of macroalgae along with their good bioconversion potential makes them a promising candidate for biofuels production. Furthermore, with defined waste management strategies, solid waste from macroalgae biomass after biofuel generation can be utilized biologically for the production of other valuable biochemicals and bioproducts. Thus, the approach appears to be conducive as it is accompanying with safe waste disposal that adds to environmental benefits. However, further research remains in the form of scaling up studies of macroalgal biomass for biofuels and value added products generation, since laboratory and demonstration trials have only proven some of the process parameters except a few case studies in pilot scale. There are certain major issues and barriers that are associated with the macroalgae based products generation process. In order to overcome such issues, new strategies along with ground research works are already underway. The major issues, barriers and research activities related to macroalgal biofuels production process are given in Table 6. One of the major obstacles in macroalgae based fuel and products generation is the occurrence of diverse form of polysaccharides and their subsequent hydrolysis to fermentable sugars (Jiang et al., 2016). Thus, there is a need to explore robust enzymatic cocktails or integrated processes to hydrolyze efficiently macroalgal polysaccahrides. Amamou et al. (2018) described a mechano-enzymatic process for polysaccharides hydrolysis. The major objective of this study was to analyze the potential of mechano-enzymatic hydrolysis of macroalgae *Gelidium sesquipedale* and *Ulva lactuca* for fermentable sugars and ethanol production. For this, an enzymatic cocktail of Haliatase which have the capability to degrade the macroalgal cell walls by hydrolyzing their polysaccharide components was utilized along with mechanical milling (vibrio ball and centrifugal milling). Upon increasing the enzyme concentration from 3.4 to 30 g/L, rate of hydrolysis increased after 72 h and subsequently enhanced the total sugars production from 6.7 g to 13.1 g/100 g biomass for *U. lactuca* and 7.95 g to 10.8 g/100 g biomass in the case of *G. sesquipedale*. The ethanol yield of 6 g/100 g total sugar was observed after 72 h fermentation for *U. lactuca*, while ethanol yield of 2 to 4 g/100 g total sugar was found best for *G. sesquipedale*. Thus, combining enzymes with mechanical fractionation is a promising approach for macroalgal biomass valorization.

13.1. Summary

Macroalgal biomass is considered as a potential biorefinery feedstock due to high growth rate and production status. Zero waste biorefinery approach can be possible by utilizing macroalgae as a feedstock. However, there are certain issues and barriers while utilizing macroalgal biomass for biorefinery purpose such as macroalgal onshore and near shore cultivation, single product formation, effective hydrolysis of diversified macroalgal polysaccharides, mixed sugars fermentation, and scaling up at large scale with wild type fermenting microorganisms. Most of the research works are on the way to resolve

Table 6
Issues and barriers in macroalgae based biofuel production technology.

Major issues	Barriers in macroalgal biofuels production process	Major research activities related to the issues and barriers	Reference
Macroalgae cultivation	High biofuel production cost through onshore and near shore farming	Macroalgae cultivation under exposed offshore conditions through offshore ring or by multi-body macroalgae farm can increase the yield of biofuels and feed production.	(Azevedo et al., 2019)
Single product generation	Biomass potential and the aspects of maximum utilization of the leftover residues are not evaluated properly.	Cascading or zero waste approach facilitates the full biomass utilization and production of fuels and other valuable biocommodities.	(Mhatre et al., 2019), (Hessami et al., 2019), (Nunes et al., 2018)
Diverse array of polysaccharides in macroalgae presents technical obstacle towards their exploitation.	Release of different monosaccharides or simple sugars from polysaccharides cannot be possible by single microbe/enzyme.	Mechano-enzymatic mode (milling and Halitase enzyme) of biomass deconstruction of macroalgae can enhance sugars production.	(Amamou et al., 2018), (Tang et al., 2017)
	Similarly, mixed sugars fermentation cannot be done by individual native organisms.	Co-fermentation of mixed sugars through more than microorganisms can increase the fermentation yield.	(Obata et al., 2016)
Pilot scale studies of macroalgal biomass for ethanol production with wild type fermenting microorganisms	Wild type fermenting microorganisms were found to be less efficient in conversion of mixed fermentable sugars to ethanol.	Utilization of recombinant fermenting microorganisms can enhance the efficiency of sugars conversion to ethanol.	(Camus et al., 2016), (Ra et al., 2014)

these issues and barriers and to make the production process even more productive.

14. Current challenges, research gap and recommendations

Macrolagae based energy and fuels generation is one of the sustainable and clean processes. However, there are few challenges that restrict its commercialization such as potential strain selection, biomass cultivation and harvesting, round the year feedstock availability, and selection of viable technology for biomass conversion. Recently, several research works reported on macroalgal cultivation, harvesting and biorefinery approaches integrated with waste valorization that addressed the above mentioned challenges and suggested commercial viability with respect to techno-economic analysis (Azevedo et al., 2019; Fernández et al., 2019; Mhatre et al., 2019; Zollmann et al., 2019; Sadhukhan et al., 2019). Moreover, there is a research gap with respect to biomass utilization for single product formation, single enzyme or conventional acid/alkali for biomass hydrolysis and laboratory scale experiments. Also, most of the zero waste cascading approaches are restricted to only laboratory scale, thus process feasibility at commercial scale is not reliable. Apart from this, solid and liquid waste recovery from each process step and its subsequent valorization along with effluents recycling are some of the few challenges which needs to be considered at pilot scale processing. In this regard, a zero waste futuristic macroalgal biorefinery approach is advised in Fig. 3 that facilitates full biomass utilization and address the key challenges for a sustainable and energy efficient biorefinery. The process also emphasizes to reuse and recycle of liquid and solid waste to value added products under a zero waste principle.

Literature reveals that futuristic macroalgal biorefinery integrated with product cascading approach and wastewater utilization will minimize the problems of environmental pollution. Whereas, co-cultivation of different macroalgae species further resolve the issue of round the year biomass availability (Fernández et al., 2019). Also, utilization of mixed biomass feedstock such as food waste, lignocellulosics, agricultural and sewage waste could enable continuous plant operation (Wang et al., 2019; Brilman et al., 2017). However, potential of mixed biomass utilization at large scale for multi-product generation should be assessed with proper techno-economic analysis. In addition, use of potential strain having auto sedimentation property further reduces the harvesting cost and use of chemical flocculants that make the process ecofriendly. In the case of biomass hydrolysis, application of enzymatic cocktails having the property to degrade a wide variety of polysaccharides will increase the yield of fermentable sugars. Moreover, co-fermentation strategy for mixed sugars fermentation is also recommended for enhanced yield of the major products. Finally, there should be specific policies on macroalgae derived fuels and products. Apart from this, there is an immense need of a healthy competition with the other seaweed products. Furthermore, a positive approach to communicating and informing the common people is indeed necessary to the achievement of this technology.

15. Conclusion and future perspectives

Exploitation of biomass sources for biofuel generation through efficient conversion technologies can transform the energy scenario. In this perspective, macroalgal biomass because of high growth rate acts as sustained feedstock reservoir for the production of bioethanol and bioproducts. The absence of lignin in their cell wall would make them a potential candidate from biorefinery point of view. The two major processes involved in macroalgal based fuel and products generation are hydrolysis of different polysaccharides to simple sugars and fermentation of simple sugars to ethanol. However, both processes have been carried out with different strategies while associated with some limitations which are being resolved through laboratory scale. There are a few studies on macroalgal biomass scaling up for bioethanol production that necessitates the implementation of biorefinery approach along with process refinement to make the whole technology feasible and ecofriendly. In this review, we have critically explained the macroalgal biomass based zero waste technology along with highlighting the role of hydrolysis and fermentation. Furthermore, we have detailed about the scaling up process of macroalgae as feedstock for biofuels and bioproducts generation which is not yet reviewed by any research groups. The issues and barriers encountered during macroalgal biomass processing for different products generation have been summarized along with possible routes or strategies to overcome such issues.

Research on macroalgae based bioethanol production has been considered as a promising technology because of carbon neutrality, high growth rate, no fertile land requirement, absence of recalcitrant lignin molecule and no input of pesticides, water and fertilizer for their growth. These advantages signify that macroalgae has considerable future prospects as a viable unutilized biomass resource for bioethanol and bioproducts generation. In the view of commercialization, biomass hydrolysis and fermentation steps have to be refined more at laboratory scale for successful scaling up at large quantity. Alternative routes or methods such as enzyme cocktail or mixed enzyme system have to be channeled for maximum biomass hydrolysis which in turn results in high alcohol content. Furthermore, the potentiality of the macroalgae biomass in terms of its broad range applications can be increased by adopting the biorefinery approach because of its wide range polysaccharide content. Thus, a next generation macroalgae based biomass processing technology can be developed to realize the hidden potential inside the macroalgae feedstocks.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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