Shifting fuel feedstock from oil wells to sea: Iran outlook and potential for biofuel production from brown macroalgae (*ochrophyta; phaeophyceae*)

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ABSTRACT

Finding renewable alternative energy resources for fossil fuels substitution has become very vital due to the serious challenges faced by humankind at present such as environmental pollution, greenhouse gas emissions, climate change, crude oil price volatility, and fossil fuels exhaustion. Macroalgae (seaweeds) are fast-growing marine plants, providing several harvests per year without the need for arable land, fertilizer, and fresh water. Various types of ecosystems like coral reefs, mangrove forests, and rocky shores can efficiently host the seaweeds production systems. These characteristics have made them highly suitable feedstocks for third-generation bioethanol production. Iran has a huge potential in renewable energy resources owing to its unique geographical location and climatic features. The country borders with the Caspian Sea in the north and with the Persian Gulf and the Gulf of Oman in the south. Seaweeds farming can also play a key role in mitigating air pollution, increasing employment rate, sustaining fossil fuel resources, bioremediating contaminated water, and improving marine ecosystem in the Persian Gulf and the Gulf of Oman. In the present article, macroalgae diversity, cultivation, and their conversion and upgrading technologies into bioethanol in Iran are scrutinized and discussed. Finally, the potential of Bushehr (the Persian Gulf) and Chabahar (the Gulf of Oman) coastlines for macroalgae cultivation is investigated. These locations receive the annual solar radiation in the range of 1680–1753 kWh/m^2 and the photosynthetically active radiation (PAR) in the range of 2.6–2.71 GJ/m^2/year with 3051–3311.9 h sunshine per annum. Furthermore, the nutrient-rich and calm water with relatively stable pH, salinity, and temperature make these coasts suitable for macroalgae farming. A potential yield up to 147–153 t/ha/year can be obtained if proper native/engineered species, well-situated sites, and compatible cultivation techniques are selected.

1. Introduction

Climatic change, energy insecurity, fossil fuel prices fluctuation, environmental pollutions, and resources depletion have spurred intense interest to seek for green and renewable energy sources [1–8]. Biofuels production from macroalgae (seaweeds) biomass by either thermo-chemical (biodiesel, bio-oil, bio-syngas, bio-crude) or microbiological (biogas, bioethanol, biobutanol) pathways can be a potential strategy to

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Abbreviation definition			
		H_3PO_4	Phosphoric acid
		KDG	2-keto-3-deoxy-gluconate
CO_2	Carbon dioxide	NaOH	Sodium hydroxide
DEH	4-deoxy-L-erythro-5-hexoseulose	PAR	Photosynthetically active radiation
DEHU	4-deoxy-L-erythro-5-hexoseulose urinate	SHF	Separate hydrolysis and fermentation
HCO_3^-	Bicarbonate	SSF	Simultaneous saccharification and fermentation
H_2SO_4	Sulfuric acid		

meet a portion of global transportation fuel demand. However, many macroalgae contain a low amount of triglyceride and a high amount of metal concentrations; the latter can catalyze or inhibit the biodiesel production processes whereas the former can deteriorate the economic feasibility of biofuel production. The high nitrogen and sulfur contents of macroalgae can also cause bioconversion complexity into biogas and bioethanol due to ammonia toxicity and high content of hydrogen sulfide and nitrogen oxides, respectively [9]. However, a high carbohydrate content of macroalgae makes them suitable feedstocks for biobutanol or bioethanol production if appropriate pretreatment, hydrolysis, and microbial fermentation methods are applied.

Currently, seaweeds are not commercially profitable biofuel feedstocks, or in some instances, not even eco-friendly, when the whole production system is taken into account [9]. With future scientific troubleshooting and progress in relevant technologies, the coastal countries can exploit this tremendous and treasured possession as a perfect feedstock for a sustainable energy development. According to the United Nation [10], the world population will hit 9.6 billion people before 2050. The World Energy Outlook 2012 [11] predicted that the world demands for renewable energy generation in order to sustain such a huge population, is expected to grow considerably.

Among various renewable energy carriers, ethanol industry has been forecasted to experience a 3.4 fold increase by 2035. The application of this green biofuel or its derivatives as blends with various concentrations in gasoline is well-known and is believed to mitigate pollutant emissions [12,13]. The conventional feedstocks for the production of ethanol are sugary or starchy biomass such as corn sugarcane, beet molasses, and potatoes, commonly referred as first-generation of ethanol production. Due to some economic and political issues like food *vs.* fuel debates, second-generation ethanol based on lignocellulosic feedstocks has been considered as a substitute for the first-generation bioethanol [14–16]. However, the current high costs of sophisticated processes used for converting lignocellulose into fermentable sugars and inefficient microbial technologies for complete fermentation of these sugars into ethanol need yet to be addressed [17,18]. Another solution may be the application of seaweeds for use as third-generation feedstock. Unlike first- and second-generation feedstocks, macroalgae prevent adverse impacts on food supplies, their cultivation does not trigger economic concerns about land management, and has no requirements for arable land, fertilizer, and fresh water resources. Compared with lignocellulose, macroalgae has almost no lignin; and therefore, their sugars can be liberated by easier and more economic operations. Chemical compositions of two brown macroalgae are compared with switchgrass and corn Stover (lignocellulosic biomasses) in Table 1.

The cultivation of macroalgae shows a relatively growing trend between 2001 and 2010 (Fig. 1) and several countries have already practiced large-scale cultivation of macroalgae. Up to 15 million metric tons of macroalgae were produced in 2010 (Table 2) [18,19] for a number of applications, including agricultural fertilizers, animal feeds, and polymers feedstock. In addition, macroalgae are extensively accepted as a food source worldwide, particularly in Asia, due to their high nutritional value. Moreover, they are attracting growing attentions in pharmaceutical industry because of the presence of bioactive compounds [20,21].

Fifty nine dry metric tons of macroalgae can be produced in each

hectare every year, and the ideal ethanol yield through the conversion of seaweeds is about 322 L ethanol/t dry macroalgae [19]. Based on this information, the estimated optimum bioethanol productivity from macroalgae is 19 m^3/ha/year. Such a yield is significantly higher than those for sugarcane (two times) and corn (five times) [18,19,24]. Brown macroalgae (Phaeophyceae) contain higher carbohydrate contents compared with green (Chlorophyta) and red (Rhodophyta) macroalgae, and can be conveniently mass-cultivated. Moreover, ethanol production can also be considered from the brown macroalgal pulp after alginate and fucoidins removal. These co-products have commercial values and the latter is utilized in the pharmaceutical industry.

In the current review, the potential of ethanol production from brown macroalgae with special focuses on cultivation, harvesting, taxonomy, chemical composition, pretreatment, saccharification, and fermentation are discussed in detail. In addition, this review summarizes the potential of brown macroalgae as feedstocks for microbial ethanol fermentation in Iran according to their diversities and distribution in the country's surrounding major water bodies (the Persian Gulf and the Gulf of Oman) and the world largest enclosed inland lake (Caspian Sea).

2. Macroalgae cultivation

Advancement in seaweeds cultivation industry has been resulted from the development of commercial market for macroalgae products in various applications. Approximately, 93% of human-consuming macroalgae comes from cultivation of four genera including *Gracilaria, Laminaria, Porphyra*, and *Undaria* [25,26]. Large brown seaweeds, commonly known as kelps, have many possible applications for humans. In the Republic of Korea, up to 60% of the *Saccharina* and *Undaria* production have been used as abalone feed [27]. Over the last two decades, *Saccharina latissima* and *Macrocystis* sp. have been cultivated in the Atlantic Ocean and eastern Pacific Ocean, respectively [28–30]. These two species are cultivated with zoospores as seeding. Although the seeding techniques are a little different in Asian and Western countries, the open water cultivation systems follow similar longlines. Recently, many efforts have been directed toward development of the seaweeds species that are resistant to diseases, stable at higher temperatures, and grow rapidly [31]. The intense selection of seaweed strains in Asia has reduced the adaptability of seaweed varieties due to

Table 1
Comparison of chemical composition of brown macroalgae and lignocellulosic feedstocks [19].

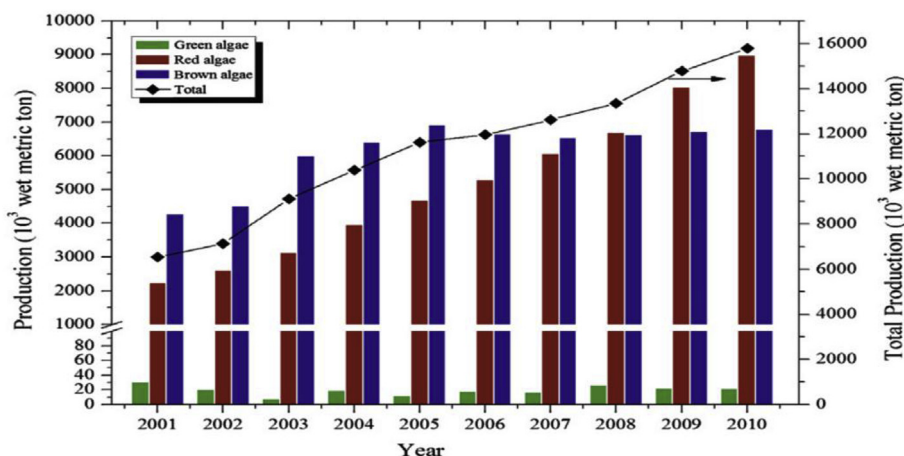| Compositions (% w/w)	Macrocystis (Brown seaweed)	Laminaria (Brown seaweed)	Summer switchgrass	Corn Stover
Water	88.2	88	13.3	6.1
Total solids	11.8	12	86.7	93.9
Ash	41.1	26	2.7	5.1
Protein	17.3	12	-	-
Lipid	-	2	-	-
Mannitol	20.2	12	-	-
Laminaran	0.8	14	-	-
Alginic acid	15.3	23	-	-
Cellulose	5.2	6	-	-
Fucoidan	0.2	5		

Fig. 1. Microalgae cultivation between 2001 and 2010 [22]. With permission from Elsevier. Copyright© 2018.

decreasing genetic diversity as well as germplasm base. In contrast, Europe and North America have mostly relied on wild sources for zoospore seeds collection [32]. The industrial production of macroalgae can be encouraged by establishing a seedbank that stores species with desirable growth and production features.

Sargassum is another genus of brown macroalgae that are extensively cultivated and used in China, Japan, and Korea for human food and medicines. Approximately, 150,000 ton of *Sargassum fusiforme* have been produced with an annual value of US $70 million in 2013 [32]. China is known as the main producer of various *Sargassum* species, including *Sargassum thunbergii, Sargassum fulvellum, Sargassum muticum,* and *Sargassum horneri.*

Macroalgae cultivation can be divided into two main phases; (i) hatchery phase and (ii) on-growing phase which are elaborated in the following subsections [33].

2.1. Hatchery production

In this phase, seaweeds seeds are cultured in greenhouses while adhered to substrates, followed by their transplantation to the coastal farms as soon as they have reached a suitable size. Hatchery production could be conducted by gametophyte seeding or direct seeding methods [33]. Prior to hatchery production, fertile seaweeds are collected in appropriate seasons depending on the species and location. Modern macroalgae cultivation technology uses artificially-produced seeds as a source of propagules. Within hatchery, the released spores (seeds) from these fertile materials are developed into gametophyte stage under controlled lab conditions. The gametophytes are then subjected to red light (minimum of 3–6 months) to further increase their density through cellular division and to avoid their fertility, which can be kept so all year round. In the gametophyte seeding method, the reproduction and growth in red gametophyte cultures must be induced by their transferring to blue light (minimum of 2–3 weeks) prior to their

spraying onto seeding substrate. NAFC Marine Center uses light intensities of circa 8 μmol/m^2/s and 50–70 μmol/m^2/s at the surface of flask for red and blue lights treatment in cultivation of brown macroalgae, respectively [34].

Alternatively, in the direct seeding method, spores are released from fertile materials directly into seawater containing seeding substrate. The facilities for both of these methods include a cold room/seawater maintained at 10 °C, equipment for releasing spore from fertile material, lights on a 12:12 light: dark cycle, nutrients, tanks to hold header rope coiled or seeders [33]. The direct seeding method is much simpler, and more economic, and less labor-intensive than the gametophyte seeding method because of the lack of hatchery maintenance phase. However, it needs more fertile materials as no bulking up of gametophyte cultures are done, has less control over the timing of seeding and deployment, and cannot maintain selected seaweeds strains for cultivation and relies on application of wild types only. The type of seeding substrate (culture string or rope) is selected based on budget and facilities. Rope is more difficult for safe transport of juveniles to sea, a lesser amount of sprayed materials can be absorbed by rope, and a larger hatchery dimensions is required. In contrast, culture string seeders/collectors require a longer preparation and deployment times and seeding directly onto them is much more complex [33]. Next to seeding, the cultures are grown under lab conditions for adequate time in seeders in the hatchery to obtain juveniles. The contamination must be avoided and hatchery environment must be kept stable during each and every step of hatchery production. The latter is essentially performed by maintaining hatchery temperature at 10 °C, checking lights for adequate lighting, keeping filters and tanks cleaned, replacing water regularly, and monitoring culture consistently. After transportation of juveniles from hatchery to sea, the hatchery instrument should be cleaned and sterilized. In the case of year-round maintenance of gametophyte cultures, they are kept in smaller cabinets to minimize the required energy and space. To discount water pumping cost, the hatchery should

Table 2
The most widely grown macroalgae in the world in 2010 [23].

Species/genus	Group of macroalgae	No. of producing countries	Quantity (kt)	Value (million US$)	Average value (US$/kg)
Saccharina/Laminaria japonica	Brown	4	5147	301	0.06
Undaria pinnatifida	Brown	4	1537	667	0.43
Sargassum	Brown	1	78	36	0.46
Eucheuma	Red	12	3748	1143	0.31
Kappaphycus alvarezii	Red	6	1875	265	0.14
Gracilaria	Red	9	1717	540	0.31
Porphyra	Red	3	1648	1163	0.71
Caulerpa	Green	1	4	3	0.59
Total			15759	4122	0.26

be placed near to the sea on flat and low-lying areas to minimize cost of water transportation by lowering energy consumption. In addition, a hatchery must sufficiently support the space required for basins, laboratory, departments, as well as the equipment [35].

2.2. On-site growing

Once juveniles with suitable size have been developed, they can then be deployed on longline or other systems at sea and left (usually 6–7 months) until harvest (around June-July) [33]. Macroalgal cultivation farms can be conducted in nearshore coastal farms, land-based ponds, and offshore farms, which basically use string or rope to attach seaweeds seedlings in lines arrangement [35]. Two common systems for macroalgae farming are vertical (hanging) and horizontal rope operations (Fig. 2). Macroalgae are fastened to the horizontal or vertical ropes attached to and suspended by the vertical rope and floats, respectively. The floats are fixed to the floor of the sea through an anchor. In the vertical system, the rope containing seaweeds is vertically linked to the weights while in the horizontal form buoyant lines are linked to each other using horizontal ropes.

Both models are designed as single raft unit (longline) or raft block (grid) in various types of seaweeds culture (Fig. 3). For this purpose, the juveniles are placed into transportation box. Generally, cool boxes lined with damp tissues are used for short distances, whereas for long journeys, large tanks are employed. At the farm site, the boat is connected to the first anchor buoy at one end of the header rope for feeding the rope through seeder. Then, the culture string is cut at the closest point to the header rope and tied around. After securing the string, the bottom of the seeder is fixed without touching the string and the header rope is passed through the seeder over the end of the boat. Finally the string is untwisted around the rope; buoys are attached to the rope at pre-marked location, and rope is dropped into water. Once the header rope is fully deployed, it is connected to the anchor buoy and the next one is started as shown in Fig. 3 [33].

2.2.1. Nearshore coastal farms

Nearshore coastal farms developed by some countries such as China, Chile, and Japan have been traditionally used for cultivation of macroalgae. However, the application of coastal areas for aquaculture is restricted in the United States and the European countries by law. In most cases, seaweeds are cultivated on ropes slung between mooring structures, named the floating raft method. This technique is not sufficiently suitable for deep water systems and is also known as a labor-intensive method [19].

2.2.2. Offshore farms

Compared with the other seaweeds species, kelp species have been known as one of the most favorable groups for offshore cultivation because they need low maintenance requirements and are easy to harvest [32]. These types of farms were introduced for the cultivation of *Macrocystis pyrifera*, commonly known as giant kelp, in Southern California nearly three decades ago. Although the structures used for algae cultivation supported the growth of kelp, they lacked the required

stability in farms structure as well as kelp attachment to them. In fact, this method not only could not provide the optimum conditions but also could not eliminate the challenges resulted from open ocean forces. On the other hand, the application of offshore farms have been successful for growth of *Laminaria hyperborean* in the North Sea [29]. Additionally, studies have revealed that *Sargassum* spp. are suitable seaweeds for offshore cultivation with a market value of $500 per ton [32]. Traditionally, cultivation of *Sargassum* species is performed using wild seedlings obtained from natural beds. Groups of seedlings were placed on ropes and subsequently attached to a longline located at a depth of 2–3 m. This method causes overharvesting of natural beds because of dependency on wild seedlings. To address this issue and also to improve the efficiency of cultivation, recyclable holdfast-derived seeding is used. After collection of seeds or seedlings by aforementioned techniques, they are seeded onto string or are attached to seed line, respectively. Thereafter, seedlings are ready for cultivation in a nursery and further outplant at sea.

There are few offshore systems that are used solely for macroalgae cultivation and most of these systems are operated in association with wind and fish farms [31]. Offshore aquaculture operations are constructed in three models: floating, anchored, and combination of both systems. Floating offshore aquaculture systems operate through wind, ocean currents, and waves. These operations often move vertically more than several meters when the sea has normal conditions and can move up and down up to tens of meter under stormy conditions. They can also be designed at the depth to overcome the storm challenges. Recently, new methods have been applied to improve the floating farms under open sea conditions that are the most successful technology in the combination of floating platform with anchored component [29]. Mostly, anchors are used to tether the system to the floor of the sea and floats. As the seaweeds cultivation at the depth of oceans is capital-intensive and labor-intensive, applying anchored systems provides benefits such as constant location, providing nutrients through passing the sea water, and washing the generated wastes. In addition, anchored operations can include nutrient upwelling pipes to fertilize low nutrient environments.

The first attempt to operate the tethered cultivation system, particularly for production of biofuels, dates back to the 1970s [36]. This system was installed for cultivation of the kelp *Macrocystis pyrifera* along Southern California coast. The plants were grown at a depth of 12 m and the system was anchored at a depth of 50 to 150 m. This first anchored offshore system provided valuable information for later works by other investigators. Ocean Spar System is a new aquaculture platform, developed by researchers in Mediterranean and North Sea through employing different methods to overcome the ocean currents challenges [31]. This system works based on USA-designed models and consists of four vertical spars for anchorage and a suspended aquaculture cage. Thoroughly, the cage can move in vertical direction and can sink below the surface of water under undesired ocean conditions. Although this system is sufficiently rigid in regions with high velocity of sea currents, but could be vulnerable to certain wind and wave conditions [31]. Another offshore cultivation system, developed in the North Sea was a longline system, which enables cultivation of multiple
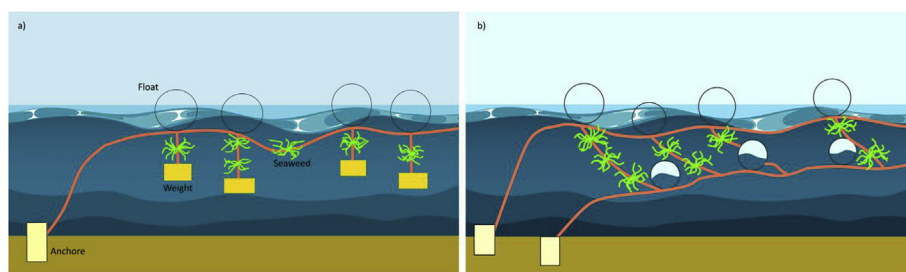

Fig. 2. Two models of rope systems, a) vertical; b) horizontal, for seaweeds cultivation. Adopted from Ref. [35].
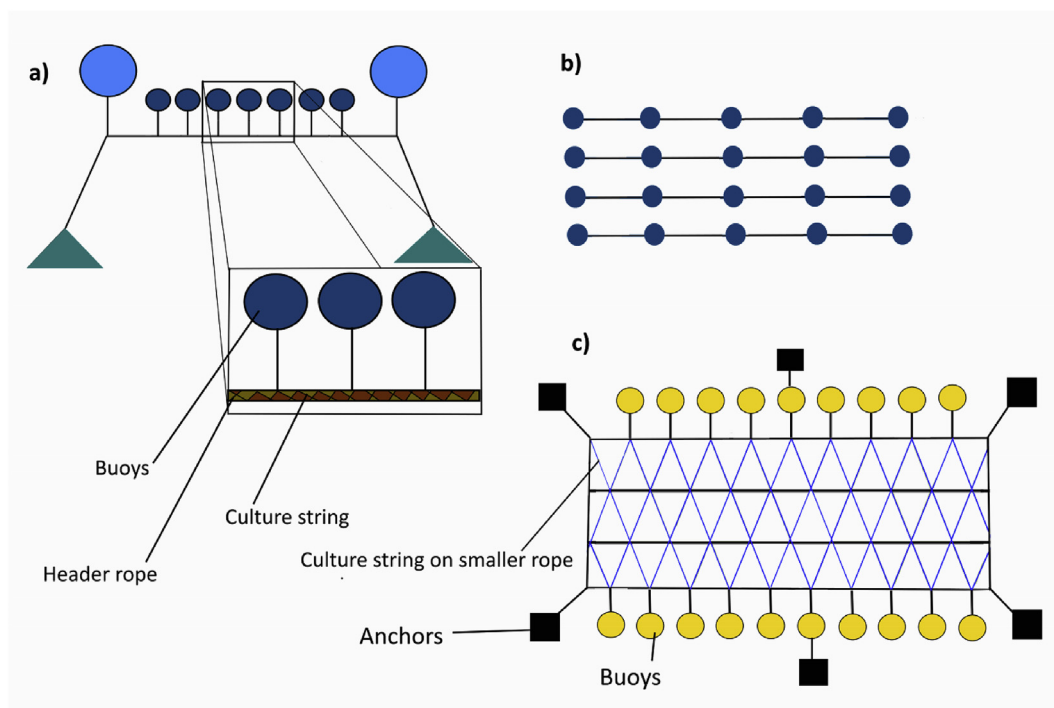
Fig. 3. Different designs for seaweed culture; a) overview of longline setup and wrapping of culture string, b) bird's-eye view of longlines design, and c) bird's-eye view of grid design. Adopted from Ref. [33].

macroalgae species [28]. The offshore ring is a more recent operation developed by Germany which showed great success for culturing *Laminaria* spp. This system is composed of a submerge ring with lines for macroalgae cultivation descending from it as well as an anchoring system and surface flotation. This system is currently under investigation, but it has high potentials for large-scale seaweeds cultivation [37].

2.2.3. Land-based pond

The application of land-based ponds along with integrated aquaculture has been tested successfully for macroalgae cultivation, in which aquaculture wastes are bioremediated and used as nutrient source for seaweed cultivation [19]. For example, salmonid fish species have been successfully used for cultivation of *Porphyra* spp., *Nereocystis luetkeana*, and *Saccharina latissima* [38]. Land-based ponds allow seaweed cultures at higher densities, compared with nearshore farms. Moreover, they present an acceptable method for cultivation of macroalgae which cannot be grown well in ocean farming. There are some advantages for land-based systems over water-based farms such as more convenient plant management; use of nutritional sources with no need for dilution; use of plants in presence or absence of holdfast structures; and avoiding open sea challenges like predation, bad weather, and diseases [39].

3. Harvesting

Macroalgae harvesting is performed by either manual or mechanized methods. The former is a common way to collect the natural and cultivated seaweeds by some instruments such as fork, net, and sickle. In contrast, the latter technique requires ships or boats and harvest macroalgae by machines equipped with rotating blades, suction, and collector [31]. For example, France uses scoubidou system to harvest *Laminaria digitata*, which is a hook-like gear equipped boat. The gear rotates and gathers seaweeds, followed by moving in the reverse direction for releasing harvested macroalgae into the boat or ship. Additionally, mechanized boats for uprooting the *Laminaria hyperborean* has also been manufactured. Such boats include a huge fork-like tool,

which traps this macroalga through targeting the seaweeds bed. Then, a crane located on the boat lifts the device that carries near to 2 ton of harvested seaweeds. Kelly et al. [40] applied a vertical wet-well attached to a hydraulic arm to gather seaweeds. This tool moves along the sea floor and harvests the seaweeds then brings up the harvested macroalgae into a net placed on the boat. The new mechanical seaweeds harvesters have been designed without the need for installation of any extra equipment such as conveyor or crane. A mowing boat, Conver C430H (manufactured by Conver, Netherlands), includes a T-front cutting instrument to harvest seaweeds. This boat with a width of 1.5 m makes the harvesting easier by allowing the operator to move along the nearer shore and to gather more seaweed in a determined time. Alpha Boats have also designed two models of harvesters, designated as SR and FX, with harvesting capacity at depth of 1.61–1.83 m and width of 1.83–2.13 m. The cutting tool of this boat is similar to combine harvester and includes two vertical cutter bars on the lateral sides of platform and the third cutter in horizontal direction. The cutters located on platform shred the seaweeds and a conveyer picks up the harvested algae on to the boat [35].

4. Macroalgae of Iran

Iran has a large climate and biological diversity. The country is located between latitudes of 25 and 40° and between longitudes of 44 and 63°. In the North, Iran has access to Caspian Sea that is the world largest enclosed body of water resource with 800 km length. However, Iran shares a larger coastline (5000 km length) in the South with two seas, the Persian Gulf and the Gulf of Oman. The former Gulf is a marine system which is economically and ecologically important for its surrounding countries. Iran is connected to Indian Ocean through the Gulf of Oman. In contrast to Iran's Caspian sea coast, the Persian Gulf and the Gulf of Oman coastlines are hot and dry which is recognized as subtropical and high-pressure zone with Coral Reefs, mangrove forests, and rocky shores [41]. Kokabi and Yousefzadi [42] reported a comprehensive checklist of macroalgae of Iran. According to their study, 309 macroalgae species, consisting of 78 Chlorophyta, 70 Ochrophyta

(Phaeophyceae), and 161 Rhodophyta have been identified in marine ecosystems of Iran (Fig. 4). Here, each family of the identified macro-algae in these three reservoirs, namely, Caspian Sea, the Persian Gulf, and the Gulf of Oman is briefly explained.

4.1. Caspian sea

There are 70 species of macroalgae in various regions of Caspian Sea as tabulated in Table 3 [43,44]. According to the diversity analysis, the Caspian Sea contains 37 species of green algae, 11 species of brown macroalgae, and 22 species of red algae as portrayed in Fig. 4 [43,44]. The dynamics for the diversity of the macroalgae species in Caspian Sea depends on variations in sea level and its salinity. For example, analyses have revealed that the prevalence of various groups of macroalgae have changed during the last years in favor of green algae, which are pre-dominant in northern Caspian Sea.

4.2. The Persian Gulf and the Gulf of Oman

4.2.1. Chlorophyta

Identified Chlorophyta of Iran consist of 78 species distributed within 20 genera including *Acetabularia, Avrainvillea, Bryopsis, Caulerpa, Chaetomorpha, Cladophora, Cladophoropsis, Codium, Derbesia, Dictyosphaeria, Halimeda, Parvocaulis, Phaeophila, Rhizoclonium, Siphonocladus, Spongomorpha, Ulva, Ulvella, Valonia,* and *Valoniopsis.* Among them, *Caulerpa* and *Cladophora* genera have the greatest variety with 12 and 13 species, respectively.

4.2.2. Ochrophyta

A total of seven families of Ochrophyta have been reported from the Persian Gulf and the Gulf of Oman with 70 species from 24 genera. These include *Bachelotia, Canistrocarpus, Colpomenia, Dictyota, Dictyopteris, Feldmannia, Hormophysa, Iyengaria, Jolyna, Lobophora, Nizamuddinia, Padina, Polycladia, Rosenvingea, Sargassum, Scytosiphon, Sirophysalis, Spatoglossum, Sphacelaria, Stephanocystis, Stilophora, Stoechospermum, Tinocladia,* and *Turbinaria.* The family Sargassaceae has been reported as the most diverse family within Ochrophyta with 33 taxa.

Table 3
Species of macroalgae identified in Caspian sea [43,44].

Chlorophyceae (green macroalgae)
Ulotrhrix flacca, U. pseudoflacca, U. implexa, U. zonata, Ulvella lens, Pringsheimiella scutata, Entocladia viridis, Acrochaete parasitica, Monostroma wittrockii, Blidingia minima, B. marginata, Ulva prolifera, U. flexuosa, U. linza, U. intestinalis, E. torta, E. ahlneriana, E. clathrata, E. kylinii, Gomontia polyrrhriza, Chaetomorpha aerea, C. linum, C. gracilis, Rhizoclonium riparum, R. implexum, R. hieroglyphicum, Cladophora sericea, C. vagabunda, C. siwaschensis, Urospora penicilliformis, Ostreobium queckettii, Chara aspera, Chara crinite, Chara foetida, Chara hispida, Chara intermedia, Lamprothamnium alopecuroides
Phaeophyceae (brown macroalgae)
Pylaiella littoralis, Ectocarpus siliculosus, E. caspicus, E. humilis, Entonema oligosporum, E. effusum, Phaeostroma bertholdii, Myrionema strangulans, Ascocyclus orbicularis, Microspongium gelatinosum, Monosiphon caspicus
Rhodophyceae (red macroalgae)
Asterocystis ramosa, Bangia fuscopurpurea, B. atropurpurea, Kylinia parvula, K. hallandica, K. virgatula, Acrochaetium daviesii, Acrochaetium thuretii, Hildenbrandtia prototypes, Lithoporella lapidea, Ceramium tenuissimum, C. diaphanum, C. elegens, Callithamnion kirillianum, Polysiphonia violacea, P. sanguinea, P. denudata, P. caspica, Lophosiphonia obscura, Laurencia caspica, Laurenciocolax polyspora, Dermatolithon capsicum

4.2.3. Rhodophyta

To date, 161 species of Rhodophyta distributed in 30 families have been identified in the southern coastlines of Iran [42]. A total of 71 genera have been reported so far. Among the three main groups of macroalgae, Rhodophyta possess the richest group based on the number of genera and species. In this group, family Rhodomelaceae with 36 taxa is characterized as the most diverse family followed by Gracilariaceae with 16 taxa [42]. Table 4 summarizes the families and genera in each group of macroalgae identified in the Persian Gulf and the Gulf of Oman.

5. Taxonomy and chemical composition of brown seaweeds

Brown macroalgae (class Phaeophyceae) taxonomically belong to the phylum Heterokonta, in which both unicellular and multicellular organisms can be found [45]. Progress in molecular biology [45–47] have provided new information about classification and evolutionary history of brown macroalgae. According to the last updated checklist of

Green Algae:
11 families, 17 genera, 37 species
Red Algae:
7 families, 13 genera, 22 species
Brown Algae:
4 families, 8 genera, 11 species

Green Algae:
15 families, 20 genera, 78 species
Red Algae:
30 families, 71 genera, 161 species
Brown Algae:
7 families, 24 genera, 70 species

Fig. 4. Geographical locations of Caspian Sea, the Gulf of Oman, and the Persian Gulf with their macroalgae number.

Table 4
The name of families and genera of macroalgae of the Persian Gulf and the Gulf of Oman.

Family	Genus
Chlorophyta (green macroalgae)	
Boodleaceae	*Cladophoropsis*
Bryopsidaceae	*Bryopsis*
Caulerpaceae	*Caulerpa,*
Cladophoraceae	*Chaetomorpha, Cladophora, Rhizoclonium*
Codiaceae	*Codium*
Derbesiaceae	*Derbesia*
Dichotomosiphonaceae	*Avrainvillea*
Halimedaceae	*Halimeda*
Phaeophilaceae	*Phaeophila*
Polyphysaceae	*Acetabularia, Parvocaulis,*
Siphonocladaceae	*Dictyosphaeria, Siphonocladus*
Ulotrichaceae	*Spongomorpha*
Ulvaceae	*Ulva,*
Ulvellaceae	*Ulvella*
Valoniaceae	*Valonia, Valoniopsis*
Ochrophyta (brown macroalgae)	
Acinetosporaceae	*Feldmannia*
Bachelotiaceae	*Bachelotia*
Chordariaceae	*Stilophora, Tinocladia*
Dictyotaceae	*Canistrocarpus, Dictyopteris, Dictyota, Lobophora, Padina, Spatoglossum, Stoechospermum*
Sargassaceae	*Hormophysa, Nizamuddinia, Polycladia, Sargassum, Sirophysalis, Stephanocystis, Turbinaria,*
Scytosiphonaceae	*Colpomenia, Iyengaria, Jolyna, Rosenvingea, Scytosiphon*
Sphacelariaceae	*Sphacelaria*
Rhodophyta (red macroalgae)	
Acrochaetiaceae	*Acrochaetium*
Ahnfeltiaceae	*Ahnfeltia*
Bonnemaisoniaceae	*Asparagopsis*
Callithamniaceae	*Aglaothamnion, Crouania*
Ceramiaceae	*Antithamnion, Centroceras, Ceramium, Corallophila, Gayliella*
Champiaceae	*Champia*
Corallinaceae	*Amphiroa, Hydrolithon, Jania, Pneophyllum*
Cystocloniaceae	*Hypnea,*
Dasyaceae	*Dasya, Heterosiphonia,*
Delesseriaceae	*Apoglossum, Myriogramme, Taenioma*
Erythrotrichiaceae	*Erythrotrichia, Sahlingia*
Furcellariaceae	*Furcellaria*
Galaxauraceae	*Actinotrichia, Dichotomaria, Galaxaura*
Gelidiaceae	*Gelidium,*
Gelidiellaceae	*Gelidiella*
Gigartinaceae	*Chondracanthus, Chondrus*
Gracilariaceae	*Gracilaria, Gracilariopsis,*
Halymeniaceae	*Corynomorpha, Grateloupia, Halymenia,*
Liagoraceae	*Dermonema, Helminthocladia, Liagora,*
Lomentariaceae	*Ceratodictyon, Lomentaria*
Phyllophoraceae	*Ahnfeltiopsis*
Rhodomelaceae	*Acanthophora, Chondria, Chondrophycus, Digenea, Herposiphonia, Laurencia, Leveillea, Lophocladia, Melanothamnus, Neosiphonia, Osmundea, Laurencia, Palisada, Polysiphonia, Zanardini, Tolypiocladia,*
Rhodymeniaceae	*Botryocladia, Rhodymenia*
Sarcomeniaceae	*Cottoniella, Platysiphonia*
Scinaiaceae	*Scinaia*
Sebdeniaceae	*Sebdenia*
Solieriaceae	*Sarconema, Solieria, Wurdemannia*
Spyridiaceae	*Spyridia*
Stylonemataceae	*Chroodactylon, Stylonema*
Wrangeliaceae	*Anotrichium, Griffithsia, Gymnophycus*

brown macroalgae taxonomy presented by Silberfeld et al. [48], 18 orders and 54 families are considered as valid names.

Macroalgae deliver 10–15% dry matter and the main source of carbohydrate (up to 60%) in macroalgae is cell wall and dehydrated algal biomass. It is worth to note that biochemical composition of macroalgae is highly dependent on seasonal variations, and geographic conditions [30,49]. An important carbohydrate content of macroalgae is polysaccharide, consisting of arabinoxylan, cellulose, galactomannan, hemicellulose, pectin, and xyloglucans, and categorizing into storage and structural polysaccharides.

Laminarin (laminaran) is the main storage starch in brown macroalgae, which is built by (1,3)-β-D-glucan with β-(1,6) branching. Residues of mannitol or glucose can be found in reducing endings. Level of branching determine the solubility of laminaran and extensively branched molecule is water-miscible, even cold water, but those with low branched is soluble in warm water only [50]. The content of laminaran in macroalgae varies with season as well as life cycle. For instance, its presence in the bladelet of *Ecklonia cava* is prominent in summer to support the production of zoosporangia during maturation [51]. In addition, it has been demonstrated that molecular weight of laminaran in young brown macroalgae, *Fucus evanescens,* is remarkably higher than laminaran in mature seaweeds [52]. Cellulose, a β-(1→4)-linked glucose residues, is one of the important structural polysaccharides in all macroalgae, especially red and brown macroalgae cell walls. Macroalgae have lower content of cellulose compared with plants. The cellulose extracted from macroalgae is categorized as porous or sponge network, which is structurally different from plants. In addition to cellulose, cell walls of most brown macroalgae, especially members of orders Fucales and Laminariales, consist of fucoidans. This sulfonated polysaccharide is crucial for embryos morphogenesis in seaweeds [53] and consists of various saccharides including (1,2)-α-L-fucose-1-sulfate, β-(1,4)-D-mannuronic acid and 3-D-xylosyl-L-fucose-4-sulfate, and (1,4)-D-galactose and L-fucosyl-3-sulfate with different degrees of sulfation. Variation in structure of fucoidans (fucoidins) and their molecular weight (43 to 1600 kDa) have been reported from different seaweeds species [50]. Similar to laminaran, the content of fucoidans is also dependent on season and age of macroalgae and is highest in October and in the matured stage. Another cell wall component in brown seaweeds is phlorotannins, which is formed from halogenated and sulfated phenolic compounds. The level of phlorotannins depends on several factors, including species and environmental conditions [54]. Other compound that is widely found in cell walls of brown macroalgae (up to 40 wt% of dry biomass) is alginic acid (alginate). This polysaccharide is composed of copolymer of two uronic acids α-L-guluronate (G) and β-D-mannuronate (M), arranged in a linear block with diverse sequences, producing uniform regions of G (poly-G) or M (poly-M) and/or their combination (poly-MG). Another significant component of seaweeds is mannitol, which is a sugar alcohol with six carbon atoms. Mannitol has various applications, particularly in food industry as sweetener. Moreover, it has been used in pharmaceutical industry as decreasing agent in cellular edema cases. The content of mannitol in macroalgae varies depending on seasonal fluctuations and maximally includes 25% of dry weight of macroalgae. The protein content of macroalgae strongly depends on season and the maximum amount of protein has been observed during spring, whereas the lowest content occurs in autumn. In addition, the amount of protein varies in different species of macroalgae approximately 2.7–21.2% which is normally higher than plants. The protein content can affect the digestion and fermentation processes of macroalgae. For example, during gasification, high content of proteins causes reduced gas formation. Moreover, it has been studied that macroalgae with high amount of protein generate toxic ammonia during biodegradation process [9].

6. Converting Brown macroalgae to bioethanol

Brown macroalgae are an untapped energy resource for production of bioethanol. However, the cell wall matrix as well as polymeric molecules must be degraded into fermentable sugars prior to microbial fermentation. Therefore, various physical, chemical, and enzymatic methods are considered in pretreatment step and subsequent saccharification step of brown macroalgae. The most common treatments are sulfuric acid (H_2SO_4) for either pretreatment or hydrolysis.

6.1. Pre-processing and pretreatment

The primary carbohydrates in brown macroalgae include alginate, cellulose, fucoidins, laminaran, mannitol (sugar alcohol); and small amounts of glucose and glyoxylic acid [19,55,56]. Macroalgae contain little to no lignin, which grants an advantage over terrestrial biomass for microbial conversion into ethanol. In this step, a number of different methods are used for pretreating large diversity of carbohydrates in macroalgae. At the end of pretreatment step, polysaccharide feedstock becomes vulnerable to quick hydrolysis and yields of monomeric sugars are enhanced. In order to make the process more effective, pretreatments must prevent degradation or depletion of carbohydrates, improve the production of sugars directly or in subsequent hydrolysis step, avoid the generation of compounds inhibiting the hydrolysis and fermentation processes, limit the energy demand, and minimize costs. Pretreatment techniques for brown macroalgae may include physical (chopping, milling, irradiation), physicochemical (hot water, steam explosion), chemical (acid) pretreatments or their combination thereof. After harvesting, seaweeds can have adhering epifauna, litter, sand, stones, or other substances. Therefore, prior to pretreatment, screening for foreign objects and debris is essential. The accuracy of this screening depends on the cultivation mode and end application [19,38]. Thereafter, it is commonly subjected to chopping and milling. These mechanical pretreatments are extensively practiced in combination with other methods and increase surface area to volume ratios. Mechanical size reduction significantly improves the sugar yield in further downstream processing; however, very fine particle size must be avoided because of consumption of higher energy and formation of clumps and channeling in the subsequent processing, for example, enzymatic hydrolysis [57]. Some of the other approaches for comminution of macroalgae include compression milling, dry milling, and wet disk milling. Generally, fermentation requires a high amount of water and, therefore, removal of water from seaweeds is not recommended due to loss of fermentable carbohydrate such as laminaran and mannitol in algal biomass. However, if long-periods or long-distance transportation is intended, the biomass is dehydrated to 20–30% of moisture content to increase shelf-life and decrease transportation costs [19,38,58].

High energy irradiations, such as gamma rays, generate ions and/or radicals in the feedstock, initiating some chemical reactions that commonly lead to chemical bond cleavages and molecular weight reduction with direct proportion to irradiation dose [59]. On the other hand, microwave oven irradiation vibrates polar bonds in the biomass and the surrounding aqueous medium, leading to generation of internal heat and a hot spot within the inhomogeneous material. The particles are exploded due to this distinctive heating characteristic, enhancing the disruption of polysaccharides in macroalgae feedstocks [60]. Yoon et al. [61] used gamma irradiation pretreatment for depolymerization of complex polysaccharides in *Undaria* sp. biomass. A jump in reducing sugar concentration from about 0.017 g/L in untreated biomass to about 0.048 g/L in gamma-irradiated brown macroalgae at the dose of 500 kGy was recorded. Moreover, up to five-time increase in reducing sugar was obtained by combining this pretreatment with acid hydrolysis (1% H_2SO_4, 121 °C, 180 min). Similarly, Yuan and Macquarrie [62] took advantage of microwave heating pretreatment for drying brown macroalga *Ascophyllum nodosum*. Then, biomass grounded and acid hydrolyzed (3.13% w/v biomass, 0.4 M H_2SO_4, 150 °C, 1 min) at the optimum temperature with the help of microwave heating, resulting in release of 127 mg monosaccharides/g of macroalgal biomass. The concentrated hydrolysate was fermented directly using *Saccharomyces cerevisiae,* which resulted in an ethanol titer of 5.57 g/L and a yield of 60.7%.

Steam explosion or autohydrolysis applies heat and pressure steam for a period of time without catalyst, followed by sudden decompression to ambient pressure. Accordingly, the individual fibers within the biomass are separated and become more accessible to acid or enzymes attack with minimum loss of material. This method is generally combined with other pretreatment techniques such as acid and hot water pretreatments. In hot water method, polysaccharides are converted into oligomers when macroalgae materials are subjected to hydrothermal pretreatment. Despite the generation of small amounts of inhibitory and toxic by-products, such as carboxylic acid and furfural, relatively high sugar recovery without acid or chemical requirements make this process ecofriendly and economical. *Padina tetrastromatica* was pretreated using hot water (121 °C, 45 min) and then enzymatically saccharified by xylanase (50 IU, pH 7, 30 °C, 6 h) obtained from *Bacillus* sp. strain BT21 [63]. The total released glucose, mannose, and xylose were 73.3 mg/g of seaweed biomass that was almost 19% higher than untreated biomass. Similarly, Soliman et al. [64] used a hot water pretreatment (pH 5.5, 0.15 MPa, 120 °C, 15 min) to provide 510 mg sugars/g of *Sargassum latifolium* biomass after biological saccharification (80% efficiency) by *Trichoderma asperellum* RM1 (30 °C, 21 day).

In acid pretreatment, polysaccharides are excessively broken to sugar monomers by dilute acid such as hydrochloric acid, phosphoric acid (H_3PO_4), or H_2SO_4. The goal of this method is to maximize conversion of polysaccharides into soluble sugars, increasing biomass porosity, and improving hydrolysis of cellulosic fractions into glucose in the upcoming enzymatic process. Up to now, dilute-acid hydrolysis is the most typical chemical method for pretreatment of raw macroalgae biomass, which is followed by subsequent enzyme hydrolysis. However, special technologies and resistant materials are required in the pretreatment reactors for industrial application of acid and heat as catalysts. At the end of this chemical pretreatment, the pH is elevated for an appropriate function of hydrolysis enzymes and microorganisms by addition of ammonia or lime. Compared with ammonia, the cheaper compound, *i.e.* lime is not an appropriate neutralizer because overliming can trigger side reactions at higher pH levels and diminish sugar concentration by 13%. Additionally, overall conditioning of the hydrolyzate slurry as well as elimination of the solid-liquid separation steps can be achieved by highly miscible neutralizer, *i.e.* ammonia.

Although most of soluble carbohydrates are washed during alginate extraction process, a valuable source of energy, *i.e.* insoluble carbohydrates are still trapped in left-over wastes. Kumar and Sahoo [65] analyzed the content of left-over pulp of *Sargassum wightii* after alginate extraction and reported almost 43–47 dry wt.% insoluble carbohydrates, 23–34 dry wt.% ash, and 5–7 dry wt.% soluble carbohydrates. Ge et al. [66] emphasized that floating residue, the waste by-product of the alginate extraction process, has 30% cellulose and 2.2% hemicellulose, making it a potential bioenergy biomass. They reported a glucose yield of 277.5 mg/g floating residue under acid pretreatment (0.1% w/v H_2SO_4, 121 °C, 60 min) and further enzymatic hydrolysis with cellulase and cellobiase (pH 4.8, 50 °C, 48 h).

Robin et al. [67] studied the diversity of monosaccharides in acid hydrolyzates of *Padina pavonica* and *Sargassum vulgare*. According to this study, the dominant monosaccharide in *Padina Sargassum* was fructose (34.30 µg/mg), followed by glucose (14.11 µg/mg), xylose (13.37 µg/mg), galactose (7.55 µg/mg) and minute total amount (13.85 µg/mg) of arabinose, glucuronic acid, mannitol, and rhamnose. The sequence was different in *Sargassum vulgare*; mannitol (49.20 µg/mg), fructose (34.30 µg/mg), galactose (9.92 µg/mg), glucuronic acid (13.22 µg/mg), galactose (9.92 µg/mg), and minute total quantity (23.76 µg/mg) of arabinose, glucose, mannose, rhamnose, and xylose. Lee et al. [68] developed an extremely low acid pretreatment method (0.06% H_2SO_4, 170 °C, 15 min) for increasing the enzymatic digestion of *Laminaria japonica*. The maximum glucan content after pretreatment was about 29%, which was 4.2 times higher than untreated biomass. They also conducted hot water pretreatment (170 °C, 30 min) as control, which released 24.8% glucan. Ravanal et al. [69] reported that the best pretreatment method for *Macrocystis pyrifera* biomass is acid pretreatment (2% v/v H_2SO_4, 120 °C, 60 min). The main carbohydrate compounds in this brown macroalga was alginate (60.6 wt%) and cellulose (22.6 wt%). Therefore, the pretreatment was followed by enzymatic saccharification of cellulose (cellulases, pH 5.2, 50 °C, 4 h) or alginate

(lyase/oligoalginate lyase, pH 7.5, 37 °C, 2 h). This process released 55.74 mg glucose/g macroalgae from cellulose and 193.7 mg uronic acid/g macroalgae from alginate. The acid pretreated and enzyme hydrolyzed of *Ascophyllum nodosum* and *Laminaria digitata* unlocked glucose (63% of total sugars) and rhamnose (55% of total sugars) as the predominant fermentable sugars from algal total carbohydrate contents, respectively [70]. Widyaningrum [71] combined acid, heat, and pressure for pretreating *Sargassum crassifolium*. This pretreatment (0.2 M H_2SO_4, 121 °C, 0.1 MPa) generated 26.68 g/L sugars, which increased to 68.32 g/L by cellulase in subsequent enzymatic hydrolysis.

Many researchers studying the acid pretreatment method also conducted hot water pretreatment as control. Hot water pretreatment delivers slightly lower concentration of sugars compared with acid pretreatment, but requires less utility and capital cost. Fasahati et al. [72] compared the cost-effectiveness of hot water with acid pretreatment method in terms of capital cost, sugar yield, and operating cost for pretreating 80,000 and 400,000 ton/year of dry brown macroalgae. They concluded that hot water pretreatment (20% solid load, 50 °C, 30 min) is economically superior over the acid thermal technique.

6.2. Hydrolysis

Next to pretreatment, algal biomass is subjected to chemical or enzymatic hydrolysis to release sugars from structural polysaccharides. If acid treatment is followed by enzymatic or microbial saccharification, it is called as acid pretreatment otherwise it is referred as acid hydrolysis. Acid hydrolysis and acid pretreatment follow same principles. Acid hydrolysis of fine-dried powder of *Colpomenia sinusa* and *Cystoseira compressa* with 5 and 3% H_3PO_4 at 21 °C for 20 min produced 0.413 and 0.305 mg reducing sugar/g dry biomass, respectively [73]. Similarly, dried-powdered biomass samples of *Padina tetrastromatica* and *Sargassum vulgare* was separately treated with 1 and 2% v/v H_2SO_4 at 121 °C for 45 min, released 0.32 and 0.44 g reducing sugars/g of dried biomasses, respectively. Arabinose was the most abundant sugar, followed by galactose and mannose, glucose, and small amounts of ribose and xylose in detoxified hydrolyzates of both seaweeds. *Saccharomyces cerevisiae* R3DSC5 converted these quantities of sugar to ethanol; the ethanol yield with *Padina tetrastromatica* was exceptionally high (0.66 g/g), unlike *Sargassum vulgare* (0.386 g/g), and was more than the other reported ethanol yield from any marine algal biomass [74]. In acid saccharification, the sugar yield is about 50% of the total dry weight of seaweeds biomass, which is about 2.5-time higher than that of enzymatic method [75]. However, the use of acid and heat lead to the formation of inhibitory compounds for microbial fermentation step. For example, despite the release of simple sugars through hydrothermal pretreatment of *Ulva lactuca*, the yield of ethanol is lower compared with mechanical pressing method [76,77]. A similar observation was recorded from heat and acid pretreated *Saccharina latissima* [78], though heat treatment is required for solubilizing laminaran. Caffeic acid, furfural, levulinic acid, and 5-hydroxymethylfurfural are originated from xylose and galactose in acid hydrolyzed seaweed biomass [79]. The enzymatic hydrolysis has some great advantages over acid hydrolysis such as milder conditions and higher yield of sugars without generation of microbial inhibitory compounds. Despite these advantages, the use of enzyme for saccharification of macroalgae is still in early stages. It needs considerable developments to cope with issues such as polysaccharide-type specific activity of enzyme and the presence of multiple polysaccharide complexes in a single species of macroalgae. Interestingly, the predominant cellulosic form in algal cells is triclinic crystalline cellulose (I α form), unlike monoclinic crystalline cellulose (I β form) that is predominant in plants. Hydrogen bonds are weaker and looser in former polysaccharide form due to the spatial arrangement of individual cellulose chains in regard to each other [80–83]. Therefore, triclinic crystalline cellulose is more conveniently converted into reducing sugars than crystalline cellulose, and is more susceptible to endocellulases and exocellulase with respect to easier access to cellulose and additional sites for attack on released fibrils, respectively. However, it is crucial to choose an appropriate enzymatic cocktail for each algal biomass to effectively degrade this polysaccharide.

Attempts to saccharify seaweed biomass with macroalgae-specific enzymes such as laminarinase were failed due to low hydrolysis efficiency. However, it was suggested that the hydrolysis efficiency could be improved by additional pretreatment or multi-enzyme complexes [22,84]. Yanagisawa et al. [85] reported an ethanol yield of more than 3% from successive enzymatic saccharification of glucan polysaccharide in Chigaiso seaweed (*Alaria crassifolia*). In this treatment, the residue-free hydrolysate from the primary saccharification was successively utilized as hydrolyzing liquid for a secondary saccharification. The resulting high titer of glucose was provided to *Saccharomyces cerevisiae* IAM 4178. The resulting ethanol concentration (5.5%) exceeds the required concentration (4–5%) for the economically feasible distillation. In another study [84], 5-cm chopped raw brown macroalgae (75% concentration) were saccharified using 1% ascorbic acid and an enzyme mixture of dextrozyme, liquozyme, rapinase, and viscozyme. After 5.5 h incubation, sugar concentration and yield was 8.8 g/L and 89.3%, respectively. Moreover, the fed-batch hydrolysis with same enzyme method generated 27.2 g/L sugar with a saccharification yield of 80.6% after 16 h. Additionally, mono-sugars can be obtained from macroalgae by a combination of chemical and enzymatic hydrolysis. This procedure was successfully applied for the production of fermentable reducing sugars, including D-galactose, D-glucose, D-mannuronate, D-xylose, L-fucose, L-glucuronate, and L-guluronate from brown macroalgae, *Laminaria* sp. and *Saccharina* sp [86].

Regardless of the methods selected, high contents of heavy metal (0.5–11% wt.) or even nitrogen, minerals, or sulfur in macroalgae may be liberated into the fermentation medium during pretreatment and saccharification steps. This highlights the need for a detoxification step before fermentation implementation, which can be accomplished by application of some materials such as activated charcoal and lime [77,79]. The mineral level as well as carbohydrates content of seaweeds can be adjusted through better understanding of their cultivation and proper harvesting time. Horn et al. [87] reported that autumn is the proper harvesting time of *Laminaria hyperborean* for ethanol production. In this season, this brown macroalga contains high levels of laminaran and mannitol, which can be easily co-fermented by *Pichia angophorae* to yield 0.43 g ethanol/g substrate. *Sargassum wightii* had the highest content of alginate and its left-over pulp during March (about 33%) and July (about 47%) in Indian coastline, respectively [65].

6.3. Microbial treatment

Microorganisms are potent cell factories for economic production of many value-added products such as various enzymes [88–90]. Seaweed-degrading enzymes are increasingly demanded for an efficient treatment of seaweed biomass. Various marine as well as algicolous fungi can degrade seaweeds as a sole carbon source by secreting alginase, amylase, fucoidanase, and other enzymes [91–94]. *Acrophialophora* sp., *Asteromyces cruciatus, Corollospora intermedia, Dendryphiella arenaria, Dendryphiella salina, Lindra thallassiae,* and *Setosphaeria rostrata* are alginase producers. In contrast, *Aspergillus flavus, Aspergillus niger, Cladosporium salinae, Curvularia lunata, Dendryphiella arenaria, Mucor* sp., *Penicillium purpurogenum,* and *Setospheria rostrata* exhibit fucoidanase activity. However, most of these fungi render weak titles of activity. Gomma et al. [94] saccharified the extracted macroalgal components and polysaccharides from the heat-pretreated *Sargassum* sp. (2% w/v dried biomass, 105 °C, 5 min) by some algicolous fungi and achieved 70% more reducing sugars, compared with pretreated biomass. In their study, *Cladosporium salinae* showed higher fucoidanase activity, whereas *Acrophialophora* sp., *Lindra thallassiae,* and *Setosphaeria rostrata* displayed higher alginase activity.

7. Bioethanol fermentation

The aim of this step is consumption of all available sugars obtained from macroalgae by fermentation for an efficient production of ethanol. Depending on the enzymatic-fermentation approach, the fermentation of the pretreated brown macroalgae biomass can be carried out either through separate hydrolysis and fermentation (SHF) or simultaneous saccharification and fermentation (SSF). SHF as the older configuration has advantages of flexibility in optimal temperature conditions for enzymatic hydrolysis of the pretreated biomass and microbial fermentation of the obtained reducing sugars. In contrast, SSF takes advantage of generation of higher yields of sugar by enzymes due to the removal of inhibitory end-products (cellubiose, glucose, xylose) through simultaneous microbial fermentation and their conversion to ethanol. In addition, an extension of the SSF method called simultaneous saccharification and co-fermentation (SECS) can be applied for a mixed-fermentation of pentose and hexoses at once [95]. The last configuration, consolidated bioprocessing or direct microbial conversion, utilized a single reactor for the simultaneous performance of enzyme production, hydrolysis of the pretreated microalgae, and ethanol fermentation. However, long fermentation process up to several days and even weeks, low ethanol yields, and high concentrations of by-products hinder the widespread application of this low capital configuration, unless recombinant microorganisms are employed [18,96]. Table 5 summarizes some above-discussed significant achievements in bioethanol production from brown macroalgae.

The advantages of any of these configurations can be exploited using different microorganisms. Two unconventional yeasts strains, *Kluyveromyces marxianus* and *Pichia stipitis* (*Scheffersomyces stipitis*) were employed for conversion of hydrolyzates of *Ascophyllum nodosum* and *Laminaria digitata* into ethanol [70]. Both of these pentose-fermenting yeasts consumed above 80% of glucose and 100% of galactose, mannose, and xylose in hydrolyzates. *Kluyveromyces marxianus*; however, showed a weak ability in degradation of fucose and rhamnose, compared with the latter yeast. Although the conversion efficiency of these non-conventional yeast was quite low (0.7–6.0 g/L), it may be surged through operating fermentation according to the physiological requirements of these yeasts. Cho et al. [97] successfully used a NaCl acclimated yeast, *Pichia angophorae* for ethanol fermentation from *Undaria pinnatifida* (sea mustard, Miyuk) slurry containing a high salt concentration. Prior to the fermentation process, the brown macroalga was subjected to acid hydrolysis (13% w/v slurry, 75 mM H_2SO_4, 121 °C, for 60 min) and finally neutralized using 5 N sodium hydroxide (NaOH) to obtain 28.65 g/L monosaccharide and 33.19 cP viscosity. They achieved a maximum ethanol accumulation of 9.42 g/L with 27% theoretical yield. SSF method was used by Jang et al. [86] to produce ethanol from *Saccharina japonica* by *Pichia angophorae*. The hot-air dried seaweed was grounded and subjected to acid pretreatment (40 mM H_2SO_4, 121 °C, 60 min). After neutralization with 5 N NaOH, the seaweed slurry was inoculated by *Bacillus* sp. JS-1 and the yeast (30 °C, 200 rpm, 136 h). This procedure resulted in sugar concentration and saccharification yield of 45.6 g/L and 69.1%, respectively. The highest concentration of ethanol was 7.7 g/L and the theoretical yield was 33.3%.

It should be noted that seaweeds contains low content of glucans, polysaccharides made from glucose; therefore, it is crucial to convert other carbohydrate components in brown macroalgae, including alginate and mannitol into ethanol. However, the mannitol catabolism creates surplus reducing equivalents, leading to an unbalanced oxidation and reduction (redox) environment during fermentation. Therefore, electron shunts, for example, micro-aerobic conditions are required for bioconversion of mannitol to ethanol. *Zymobacter palmae* can metabolize mannitol under semi-fermentative conditions and produce ethanol with a yield of 0.38 g/g mannitol [87]. Kim et al. [98] used ethanologenic recombinant *Escherichia coli* KO11 for SSF of the acid-pretreated *Laminaria japonica*. The hydrolysate contained a little less than 7% glucose and 30.5% mannitol. The recombinant bacterium was able to convert these reducing sugars in hydrolysate into ethanol (0.4 g/g carbohydrate) when Luria-Bertani medium and hydrolytic enzyme, *i.e.* laminarinase were added. Alginate is found in high concentrations (up to 40 dry wt.%) in brown macroalgae and are resistant to fermentation because of the generation of pyruvate as the end product favored by redox balance [19,99]. Compared with mannitol, two reducing equivalents are required for fermentation of each mole of alginate into ethanol. Hence, the catabolic pathway of alginate supplies an extra sugar source as well as a counterbalance to the surplus-

Table 5
Pretreatment, hydrolysis, and fermentation of some brown macroalgae feedstock into ethanol.

CC[a]	Pretreatment-Hydrolysis	Sugar content	FC[b]	Microorganism	Ethanol Concentration	Yield-Theoretical yield
Ascophyllum nodosum						
44.7%	Mechanical-Microwave assisted acid	0.127 g/g	SHF[c]	*Saccharomyces cerevisiae* 37 °C, 72 h	5.6 g/L	20.9 mg/g biomass-61%
57.84%	Chemical-Enzyme	15.45 g/L	SHF	*Scheffersomyces stipitis* 30 °C, 144 h	2.4 g/L	7.75 g/L
				Kluyveromyces marxianus 30 °C, 30 h	0.7 g/L	4.06 g/L
Laminaria digitata						
64.47%	Chemical-Enzyme	29.3 g/L	SHF	*Scheffersomyces stipitis* 30 °C, 144 h	5.8 g/L	12.92 g/L
				Kluyveromyces marxianus 30 °C, 30 h	6 g/L	10.25 g/L
Padina tetrastromatica						
32.05%	Mechanical-Acid	0.32 g/g	SHF	*Saccharomyces cerevisiae* R3DSC5 30 °C, 72 h	10 g/L	0.66 g/g of biomass
Saccharina japonica						
66.0%	Mechanical-No	-	CBP[d]	Recombinant *Escherichia coli* 25–30°C, 72 h	4.7 v/v%	0.281 g/g of biomass-80%
66.0%	Chemical-Microbial	45.6 g/L	SSF[e]	*Bacillus* sp. JS-1 (saccharification) *Pichia angophorae* (ethanologenation) 30 °C, 136 h	7.7 g/L	33.3%
Sargassum vulgare						
52.84%	Mechanical-Acid	0.44 g/g	SHF	*Saccharomyces cerevisiae* R3DSC5 30°C, 72 h	7.6 g/L	0.38 g/g of biomass
Undaria pinnatifida						
48.5%	Mechanical-Acid	28.65 g/L	SHF	*Pichia angophorae* 30 °C, 72 h	9.4 g/L	27%

[a] Carbon content.

reducing equivalents generated by mannitol. These allow simultaneous fermentation of all three sugar sources in brown macroalgae for ethanol production [18]. However, important ethanologenic microorganisms are inefficient in alginate fermentation; therefore, one solution is the conversion of alginate into oligosaccharides using partial acid and alkali hydrolysis or microbial-derived alginate lyase. Unfortunately, chemical hydrolysis of alginate has various economic, environmental, and technical obstacles. On the other hand, the commercial enzymatic breaking down of alginate is not possible due to lack of inexpensive enzymes. Alternatively, the commercial value of alginate can be exploited by its separation before ethanol fermentation. Sudhakar et al. [100] reported that despite higher content of total carbohydrates of some fresh brown macroalgae, probably *Sargassum ilicifolium* and *Sargassum wightii,* biosaccharification of the acid-pretreated spent-seaweeds from alginate industry resulted in release of more reducing sugars. The ethanol production costs can be reduced by selling alginate as a co-product in existing market. In contrast, to achieve the full ethanol potential from brown macroalgae, the alginate must be somehow assimilated by ethanologenic microorganisms. Pursuant to this approach, recombinant engineering aims to develop microorganisms with superior efficiency in conversion of alginate into ethanol. A number of microorganisms encode alginate lyases that catalyze the formation of oligomers by depolymerization of alginate through an endolytic *β*-elimination reaction. Subsequently, oligoalginate lyase cleaves these oligomers *via* exolytic mode and degrades them into unsaturated monomers. The resulting monomers are spontaneously reorganized into 4-deoxy-L-erythro-5-hexoseulose (DEH) [18,101,102]. DEH is subsequently reduced into 2-keto-3-deoxy-gluconate (KDG) by catalytic action of DEH reductase. Through Entner-Doudoroff pathway, KDG is converted into pyruvate and glyceraldehyde-3-phosphate by KDG kinase and KDG-6-phosphate aldolase, respectively [18,103,104]. A homoethanol engineered pathway was described in the alginate-assimilating bacterium *Sphingomonas* sp. A1. This bacterium was created by Takeda et al. [105] and was able to uptake whole polyuronic acid alginate and degrade and transform it into ethanol within the cytosol. Within three days, this ethanologenic recombinant utilized 87% of sodium alginate and accumulated 13 g/L ethanol with conversion efficiency of 54%. Similarly, Wargacki et al. [18] inserted a 36-kilo-base pair DNA fragment containing a system for extracellular alginate depolymerization from *Vibrio splendidus* into an engineered *Escherichia coli*. The inserted fragment encoded enzymes responsible for alginate transport and metabolism. Therefore, the recombinant bacterium was able to simultaneously depolymerize (extracellularly), uptake, and consume alginate to form 4.7 v/v% ethanol with an ethanol yield of 0.281 g/g untreated dry macroalgae (*Saccharina japonica*). More recently, a DEH urinate (DEHU) transporter was identified from alginolytic eukaryote *Asteromyces cruciatus,* inserted, and overexpressed in *Saccharomyces cerevisiae* [106]. This alginate transporter, together with the essential bacterial alginate genes as well as deregulated native mannitol catabolism genes makes co-fermentation of DEHU and mannitol (1:2 molar ratio) by *Saccharomyces cerevisiae* BAL2956 possible. At total sugars concentration of 6.5%, ratio of mannitol to DEHU consumption, ethanol concentration, and maximum theoretical yield were 2.4, 3.3 v/v%, and 83%, respectively. When the total sugar concentration was increased to 9.8%, these numbers changed to 2.1, 4.6 v/v%, and 75%, respectively. These studies highlight that all the dominant carbohydrates content in brown macroalgae can be utilized as substrates for ethanol production. Therefore, ethanol concentrations close to the benchmark titers for economic lignocellulosic and cellulosic ethanol fermentation can be achieved. Moreover, Camus et al. [107] examined the feasibility of the bioethanol production based on *Macrocystis pyrifera* farming and its conversion by a genetically-modified *Escherichia coli* in a 75 L fermenter. They scaled up the bioconversion procedure through a four-stage process model to produce 0.213 g bioethanol/g dry brown macroalga with 64% theoretical yield of ethanol, which was equal to 9.6 m³ of ethanol/hectare/annum. The

process included acid leaching for removal of large quantities of potassium chloride, depolymerization of the leached seaweed for enzymatic hydrolysis of alginate, saccharification of the depolymerized liquid for degradation of oligoalginate into DEHU (22.3 g/L), and fermentation (200 rpm, 25 °C, 141 h).

8. Potential environmental challenges

Despite various benefits of macroalgae, particularly brown macroalgae, to produce biofuels, there are some potential environmental challenges that must be considered. For example, a substantial expand in seaweeds farms is required to quench the high global demands for fuels. This intensive cultivation of macroalgae may pose marine and coastal environment at some risks, including changes in natural habitats, water hydrology characteristics, and nutrient content of marine ecosystems. It can also modify the biodiversity of seagrasses and mangroves which usually have inverse proportion with seaweeds cultivation [58]. Additionally, some environmental issues, such as interruption in wildlife, may be occurred because of seaweeds harvesting. Sometimes, overharvesting especially using mechanical instrument decreases the biodiversity of the sea [35].

9. Potential of Iran in bioethanol production from Brown macroalgae

In this section, two points (one for each water body) in the Gulf of Oman and the Persian Gulf are investigated as the representative of that particular water reservoir for potential of macroalgae farming. In contrast, the cultivation of macroalgae in Caspian Sea currently is not possible due to socio-political obstacles in the coastal zone as well as some unresolved political issues regarding the share of Iran from Caspian Sea.

9.1. Oceanographic characteristics of the Persian Gulf at Bushehr coastline

The Persian Gulf has the maximum width, length, and depth of 180 miles, 615 miles, and 93 m (mean 36 m), respectively. This semi-enclosed water is connected to the Gulf of Oman through only one narrow 35-mile-wide opening, Hormuz Strait. Therefore, the highest salinity (41 psu) and highest water temperature (37 °C) of the Persian Gulf are higher than open seas. However, the large amount of evaporation as well as higher salt concentration generates counter-rotating gyres parallel to Iranian side from Indian Ocean to the Persian Gulf through the Gulf of Oman (Fig. 5). This current provides cooler and nutrient-rich fresh water, which causes Iran coastlines experience lower salinity and water temperature than southern Persian Gulf countries. The velocity of water in the Persian Gulf is very low and is about 10 cm/sec with weak tide of maximum 1.6 m.

Bushehr coastline experiences a water temperature range of 15–34 °C with less than 1 mm precipitation. In late winter (February-March), the water temperature is 18–20 °C, which increases to 32–34 °C toward the end of summer (August-September). Surprisingly, the salinity and evaporation are maximum in winter rather than summer [109]. The combination of cooling, evaporation, and salinity forms vigorous vertical mixing that totally overturns the water column in February. In contrast, the surface water is becoming warm in summer, decreasing the water density and stabilizing it. However, surface water density is increased due to evaporation and causes an unstable overturn that with lower thermocline influences water less than 20 m [108]. The most well-known wind is Shamal (Fig. 6), a year round northwest wind, which usually has not 10 m/s speed and lasts several days during winter, but continues from early June through July during summer [110].

The consistent residual circulation (wind- and density-driven) significantly contributes in moving surface pollutions (such as oil) to the Arabian Peninsula beach and finally removing them from the Persian

Fig. 5. Surface currents and circulation processes within the Persian Gulf and Gulf of Oman. Adopted from Ref. [108].
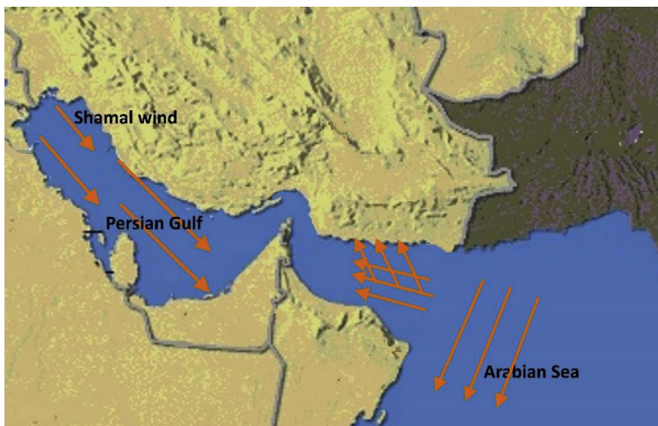

Fig. 6. Dominant wind directions in the Persian Gulf, the Gulf of Oman, and northern Arabian Sea.

Gulf, Hormuz Strait, and the Gulf of Oman [108]. The region has arid condition and clear sky as a result of descending dry air. Rahimzadeh et al. [111] measured the seasonal mean of sunshine hours for the period 1981–2007. It was found that Bushehr province receives a total of 3051 h sunshine/annum, of which, respectively, 844.9 h, 923.3 h, 681.5 h, and 601.3 h occur in spring, summer, autumn, and winter. According to Solargis, the region is absorbing an average annual sun of

about 1680 kWh/m^2 (Fig. 7), which roughly deliver 2.6 GJ/m^2/year PAR. Moreover, the highest energy conversion yield of C3 photosynthesis is 11.6–12.6% (30 °C, 380 ppm CO_2), which drops to 4.6% after photorespiration and respiration [112,113]. Therefore, a yield up to 147 t/ha/year can be generated, which is 12 and 68% higher than those obtained in Spain and Denmark, respectively [113]. This is roughly equal to the average potential yield (127–175 t/ha/year) from microalgae production by raceway pond and photobioreactor II [114]. Some other characteristic related to water nutrients have been provided in Table 6.

9.2. Oceanographic characteristics of the Gulf of Oman at Chabahar coastline

Similar to Bushehr, Chabahar has clear sky and arid conditions but receives 8.37% more hours of sunshine (3311.9 h/annum). Of these, 900.5 h, 987.1 h, 761.4 h, and 663 h occur in spring, summer, autumn, and winter [111]. Therefore, an average annual sun of 1753 kWh/m^2 (Fig. 7), PAR of 2.71 GJ/m^2/year, and biomass potential yield of 153 t/ha/year are expected. This amount of biomass is 3.6- and 5.4-time higher than the average yields of sugar beets and potatoes [115]. The ranges of water temperatures, pH, and salinity are 19.5–33°C, 8.1–8.4, and 36.4–37.2 psu, respectively (Fig. 8). The temperature range is quiet stable and shows only 4.7 points fluctuation from November to April and another 3.5 points fluctuation from May to October (excluding August, 33 °C) (Fig. 8C).

The difference in land-sea latent heat generates summer and winter monsoons that significantly impact circulation pattern over the Gulf of Oman and the northern Arabian Sea. The latter is the persistent northeasterly wind that starts from November to April with an average speed of less than 5 m/s. In contrast, the former is more energetic (15 m/s) with south and southwest directions, contributing to ocean circulation as well as biogeochemical processes in the region [116]. However, the dominant wind directions in the Gulf of Oman and Northern Arabian Sea are westerly to northwesterly and southwesterly, respectively, as shown in Fig. 6 [116]. Moreover, the Persian Gulf also contributes to the exchange of water between the Gulf of Oman and Indian Ocean (Fig. 5). Some water nutrients of this location have been presented in Table 6.

9.3. Brown macroalgae farming in the Persian Gulf and the Gulf of Oman

A number of key parameters must be considered for large scale, sustainable cultivation of macroalgae, including sunlight availability, climate, water depth and physicochemical characteristics, water circulation patterns and velocities, and nutrient availability.

Macroalgae mainly require calcium, carbon, magnesium, nitrate, phosphate, and potassium for good and healthy growth. Nitrogen, phosphorous, and silicon are well-known micronutrient elements,
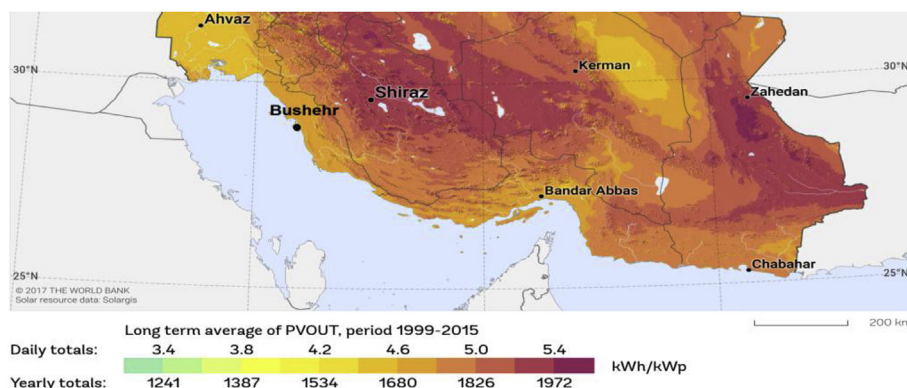

Fig. 7. Average annual sun on Southern coastlines of Iran. Courtesy of Solargis, https://solargis.com/.

Table 6

Concentrations of some micronutrients in the Persian Gulf and the Gulf of Oman water.

Water reservoir	Phosphate[a]	Nitrate[a]	Silicate[a]	Nitrite[a]	Ammonia[b]	Bicarbonate[c]
The Gulf of Oman	0.57	0.78	6.37	0.475	0.87	47.7-130
The Persian Gulf	0.37	0.29	4.2	0.355	0.81	47.7-130

[a] μmoles/L.
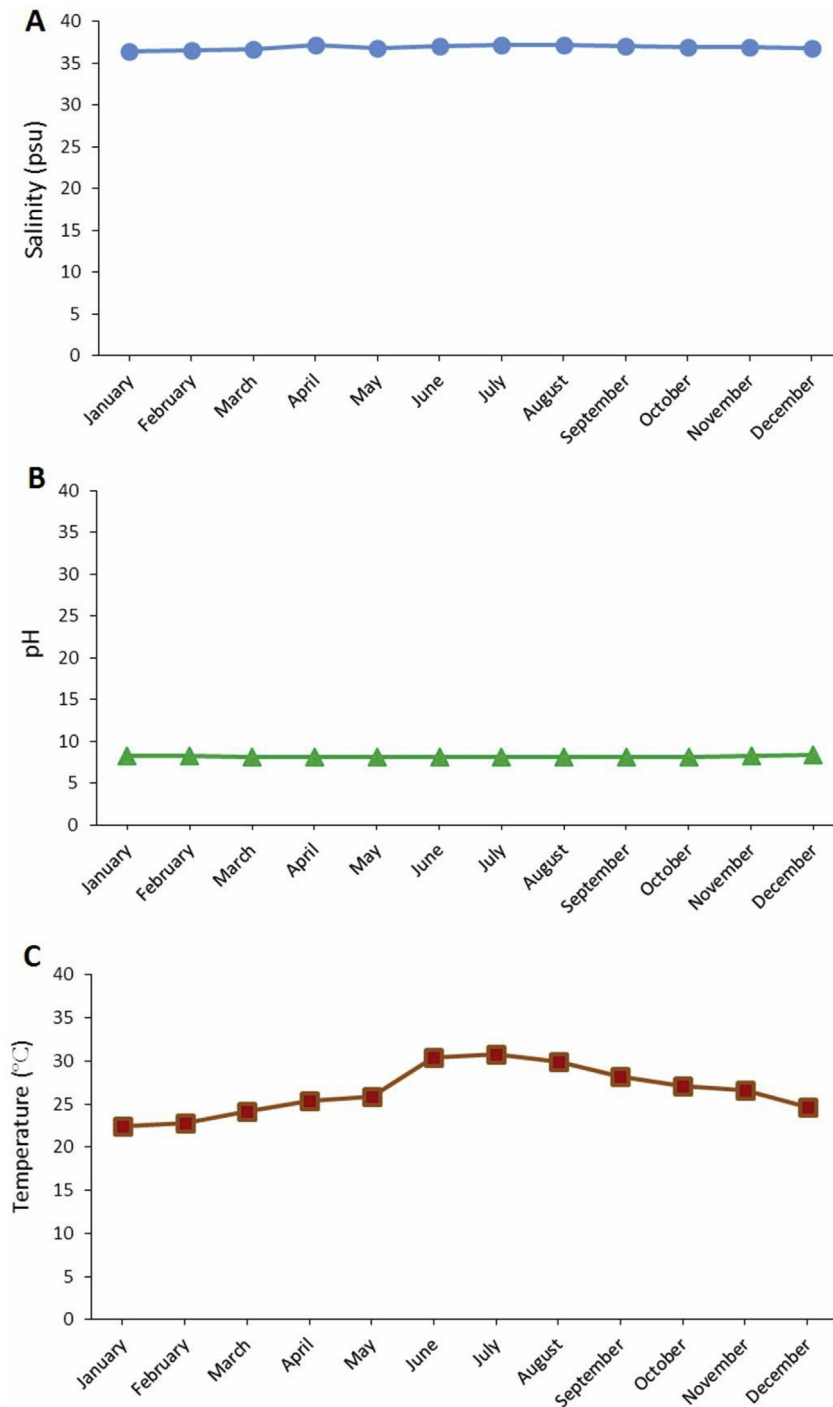[b] μg/L.
[c] mg/L.

Fig. 8. Yearly fluctuations of A: water salinity (psu), B: water pH, and C: water temperature in Chabahar coastline.

which recognized as an index of potential fertility of seawater. The atomic ratios of phosphorous:nitrogen:silicon in water of the Persian Gulf and the Gulf of Oman are 1:2.2:11.1 and 1:2.7:11.8, respectively [117]. As the ratio of inorganic nitrogen/phosphate was lower than the standard Redfield atomic ratio of 15:1, therefore, nitrogen is more important for macroalgae growth as a limiting nutrient in both Gulfs and denitrification process dominated nitrogen fixation [118]. The concentrations of inorganic phosphate, nitrate, and silicate were 0.57, 0.78, and 6.37 µmoles/L in the Gulf of Oman whereas their concentrations were 0.37, 0.29, and 4.2 µmoles/L in the Persian Gulf water as summarized in Table 6 [117]. Similarly, both Gulfs had high cations and anions concentrations (mg/L) including bromide (0.072–0.078), calcium (316–678), carbonate (154–160), magnesium (173–555), nickel (0.312–0.324), potassium (1341–1915), sodium (7646–9902), strontium (5–6), sulfate (1725–3060), and sulfur (575–1020) [119]. The presence of these nutrients as well as some minor concentrations of copper, iron, lithium, manganese, molybdenum, zinc, and zirconium provide a rich medium for seaweeds cultivations in this region. However, the water sample were collected near Qeshm Island (Hormuz Strait); therefore, lesser concentrations of these elements are expected in the northern Persian Gulf at Bushehr location and the northern Gulf of Oman at Chabahar location. Another important requirement for macroalgae photosynthesis is inorganic carbons, in the form of CO_2 and bicarbonate (HCO_3^-), which is in association with pH. When there are adequate amounts of CO_2 and HCO_3^-, most of seaweeds can grow in pH values ranging between 7 and 9 (optimum pH in the range of 8.2–8.7) [120]. Bushehr location (at the Persian Gulf) has pH of 7.9–8.1 whereas Chabahar location (at the Gulf of Oman) has more alkaline pH range of 8.1–8.4. It is believed that both Gulfs have relatively same concentration of HCO_3^- (47.7–130 mg/L). The dissolved concentrations of HCO_3^- shows consistent increase in both Gulfs due to an increase in atmospheric CO_2 level as well as lack of dense terrestrial vegetation in the region. Therefore, regional CO_2 sequestration probably occurs through oceanic sequestration in these two main water bodies of the region in the form of HCO_3^- (90%), CO_3^{2-} (9%), and dissolved CO_2 (1%). CO_2 enrichment threats the marine ecosystem such as Coral Reefs or shells by ocean acidification phenomenon. This phenomenon has probably caused the worst adverse effect on the Gulf of Oman than any other water body in the world. It is believed that the largest marine dead zone is within the Gulf of Oman because of (i) running off agricultural effluents containing nitrogen and phosphorous from the land, (ii) very slow movement of water, and (iii) low oxygen concentrations in the water streams entering it. Macroalgae farming may partially address this oxygen depletion phenomenon by remediating these pollutions and increase dissolved oxygen in the region. The best out of ocean acidification can be exploited by establishing macroalgae farming in the region, providing biofuels while simultaneously decreasing the aqueous CO_2 concentration, bioremediating pollutions, and increasing pH of water.

At the time, no comprehensive information about the temperature requirements of macroalgae inhabiting in warm water is available. Browsing literature only provide scattered information about growth temperature requirements of some cold water macroalgae, such as those in Baltic Sea and Atlantic or Pacific Oceans, and warm water inhabiting macroalgae are totally undermined. However, it worth to mention that the growth of many cold-water macroalgae stops and they start deteriorating as the temperature goes higher and these macroalgae, unlike those macroalgae that are found in warm water, have adapted to low temperatures. Altamirano et al. [121] found a relationship between temperature and UV irradiation on growth of germlings in three *Fucos* spp. It was reported that a combination of high ultraviolet-B radiation with high temperature (16 °C) can be detrimental. Another study observed rapid degradation of *Macrocystis* spp. rafts above 20 °C in Chilean Pacific coast [122]. Additionally, combination of high CO_2 and high temperature (20 °C) drastically decreases biomass formation and have influence on productivity and respiration rates of *Sargassum muticum* and *Cystoseira tamariscifolia* [123]. In contrast, *Sargassum horneri* can optimally grow (4.6% each day) at 1 *m* water depth at 25 °C [124]. A significant decline was observed in Florida macroalgae at the temperatures higher than 31 °C [125]. Ukabi et al. [126] found some green seaweeds (*Caulerpa* spp.) that continued growing at temperatures up to 31.5–32.5 °C in Mediterranean Sea. Similarly, Anderson [127] reported brown (*Dictyota menstrualis, Sargassum fluitans*) and red (*Laurencia chondroides*) macroalgae that showed stable net primary productivity at 32 °C. Surprisingly, most tropical marine seaweeds have optimum development at 31–32 °C, the temperature close to their lethal and sublethal points (about 32–38 °C) [128]. A systematic study of the native brown macroalgae temperature thresholds in the Persian Gulf and the Gulf of Oman may nominate high temperature- and radiance-resistant species for their exploitation in bioethanol production. Such a study can even help understanding the mechanisms of adaptation and interaction with a high dissolved inorganic carbon in macroalgae. This information are vital for not only sustainable cultivation of macroalgae in Iran but also across the globe when an increase of up to 4 °C in sea surface temperatures is expected by the end of this century. Interestingly, some brown macroalgae, for examples *Undaria* spp., require lower irradiance and light:dark ratio (8:16 h in these examples) for growth of gametophytes, whereas their growth and maturation are density-dependent in day lengths of 16:20 and 12:12, respectively [129].

Plants, including macroalgae, adsorb sunlight in wavelength of 400–700 nm for photosynthesis, called PAR, which accounts for about 43% of the total incident sunlight. Iran locations on world Sun Belt (Fig. 7) as well as the access to nutrient-rich calm and clear water in

Table 7

Comparison of geographical parameters for the Bushehr coastline in Persian Gulf and Chabahar coastline in the Gulf of Oman.

Geographical Parameter	Bushehr	Chabahar
Climate	Hot and dry, less than 1 mm precipitation, clear sky	Arid conditions with clear sky
Sunlight	3051 h of sunshine/annum	3311.9 h of sunshine/annum
	Average annual sun of 1680 kWh/m²	Average annual sun of 1753 kWh/m²
	PAR[a] of 2.6 GJ/m²/year PAR	PAR of 2.71 GJ/m²/year
Wind	Shamal- northwest wind (≤ 10 m/s)	Northeasterly wind (≤ 5 m/s)
		South and southwest directions (≤ 15 m/s)
Water depth	93 m (mean 36 *m*)	Up to 3500 m (Up to 2000 *m* in Iranian side)
Water circulation and pattern	Counter-rotating gyres parallel to Iranian side from the Gulf of Oman to the Persian Gulf	Counter-rotating gyres parallel to Iranian side from Indian Ocean to the Gulf of Oman
	10 cm/sec, weak tide (1.6 *m*)	
pH	7.9–8.1	8.1–8.4
Salinity	37.15–43.95 psu (41 psu at Bushehr)	36.4–37.2 psu at Chabahar
Temperature	15–34 °C	19.5–33 °C
Potential yield	147 t/ha/year	153 t/ha/year

[a] Photosynthetically active radiation.

both Gulfs provide good conditions for brown macroalgae cultivation. The seasonal water temperature variation is low and nutrient is available year round. Also, the lack of storm minimizes the complications in infrastructures such as entanglement of lines, culture string breaking, or loss of buoys. Table 7 compares Bushehr and Chabahar coastlines in respect to their geographical parameters.

Although both Bushehr and Chabahar show acceptable physical factors for macroalgae cultivation, the latter location provides more favorable PAR pH, salinity, and water temperature. Both locations partially fulfills the socio-political factors critical to macroalgae cultivation practices; low population and recreation centers due to arid conditions, no military sites, and unsuitable for production of marine energy (such as tidal and wind power). However, the Persian Gulf is a significant economic hub for gas and oil production, causing dense tankers traveling through this relatively narrow Gulf. The shipping lanes, together with tens of offshore platforms complicate the dedication of specific location in the Persian Gulf for macroalgae cultivation. Moreover, these two factors continuously introduced an unknown amount of pollutants, particularly oil, into water. Therefore, farming macroalgae as animal feed or human food is not possible. Alternatively, the sustainable cultivation of macroalgae can be exploited for biofuel production if careful survey regarding species and their physiological adaptations are conducted. The most physical limiting factor, particularly in the Persian Gulf, is high temperature in summer months (August-September) that is up to 34 °C. However, many harsh physical conditions in the region can be overcome with better knowledge about warm-inhabiting macroalgae, their depth requirements and threshold (for temperature and radiance adjustments), adapting modern science and technology for more efficient cultivation, and pinpointing the time of harvest or several harvest in a year for maximum yield of biomass before deterioration of the macroalgae in seawater. At the end, advances in pretreatment, saccharification, and fermentation technologies can improve the feasibility and benefits of macroalgae cultivation for biofuel production in Iran, which of course needs the support of policy makers to compete with fossil fuels as well.

10. Conclusions

Iran has a high macroalgal biodiversity in marine ecosystems, particularly, in the Persian Gulf and the Gulf of Oman. There are 379 out of 6200–13,248 species of macroalgae in coastlines of Iran, out of which 81 are brown macroalgae. Among the various brown macroalgae identified in Iran, two native genera, *Padina* and *Sargassum,* have a great potential for bioethanol production. According to the macroalgae diversity studies, there are 10 species of *Padina* in the Southern coast of Iran including *P. australis, P. boergesenii, P. boryana, P. distromatica, P. dubia, P. glabra, P. gymnospora, P. minor, P. pavonica,* and *P. tetrastromatica*. One of the main important components of brown macroalgae is alginate, which can be targeted in the pretreatment, saccharification, and fermentation processes for bioethanol production. It has been documented that *Padina* spp. have high amounts of carbohydrate, making it an excellent feedstock for bioethanol production. Similarly, genus *Sargassum* is widely distributed in the tropical and subtropical regions. To date, 25 out of 300 valid species of *Sargassum* have been identified in the Persian Gulf and the Gulf of Oman, making Iran as a rich resource of this potent brown macroalgae genus. Chemical analyses of *Sargassum* spp. biomass showed that they contained a high amount of carbohydrate as the total hydrocarbons has been estimated to be 47.06% on dry basis. Appropriate species can be cultivated in the southern coastlines of Iran since these locations have a good solar radiation, tropical climate, and stable conditions. This provides various socio-economic advantages for Iran by reducing air pollution, unemployment rate, reserving fossil fuels, and even bioremediating water pollutions. In fact, wastewater treatment could be well integrated with liquid biofuels production. Under this scenario, the organic contents of wastewater could be utilized by macroalgae species cultivated in land-based ponds (Section 2-2-3) to generate carbohydrates and lipids that could be subsequently converted into bioethanol (Section 6) and biodiesel, respectively. It is worth quoting that through this strategy, the downstream treatment of the resultant slurry by membrane-based technologies such as membrane bioreactors could be facilitated. More specifically, the decreased amounts of organic contents (carbon and nitrogen) lead to lower production of soluble microbial products and extracellular polymeric substances and therefore, less membranes fouling and higher membranes efficiency [130]. However, the species, cultivation techniques, harvesting techniques, and optimal localities must be carefully studied and determined for unlocking this tremendous and treasured possession for Iran national benefits. Moreover, the joint contemplation of some factors such as farms scale, environmental conditions, and impact on ecosystem should be considered. The distance between hatchery and macroalgae farm should be minimized to reduce the environmental impacts related to the use of fossil fuel. Additionally, the electricity obtained from renewable sources like solar systems can be used in hatchery (cooling water, lighting, *etc.*), transportation (juvenile, seaweeds biomass, *etc.*), and on-site growing (juvenile deployment, seaweed monitoring, harvesting, *etc.*). Furthermore, these renewable energies can then be employed in the subsequent pretreatment, hydrolysis, fermentation, and even distillation processes. Therefore, extensively available solar energy can be indirectly embodied in the produced bioethanol. Conversion of solar energy into bioethanol through macroalgae cultivation is more feasible and profitable in Iran compared with many countries receiving little solar radiation. For example, in the North sea off Germany 60–70 t/ha/year biomass of *Saccharina latissima* is possible, which is about 2.1–2.5 times less than possible macroalgae biomass yield in the southern coast of Iran. Similarly, more growing months is possible in the southern coastlines of Iran owing to more stable and warm conditions when compared with European countries such as Denmark (up to six months growth). Again, this advantage let Iran have up to 6.6–7 times higher yield than those countries with less months of growth. However, it is vital that the most appropriate species are selected or developed and the required technologies and infrastructures are carefully investigated.

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