High-value chemicals from marine macroalgae: opportunities and challenges for marine-based bioenergy development

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Abstract. Marine macroalgae (seaweeds) are considered as one of the potential alternative sources for producing energy. Their low lignin and high carbohydrate content have often attracted much attention on the synthesis of alcohols as well as gaseous fuels, although these developments are limited by the low economic value of fuels. Marine macroalgae contain chemical that are distinctively different compared with terrestrial biomass. Their organic chemicals, either carbohydrates or secondary metabolites, are usually unique and vary depended on the diversity of marine macroalgae. These features offer great opportunities for the production of various marketable products with higher economic value than fuels. Integration of their valuable non-energy bioproducts will provide a financial incentive to reduce the cost production of bioenergy from macroalgae. In this review, we present the potency of high-value chemicals that can be derived from marine macroalgae. Current states of the biorefinery researches of this marine biomass are also discussed together with the challenges on their large scale application.

1. Introduction

High growth energy demand, fast depleting fossil fuel sources and global climate change always encourage the search on alternative renewable and sustainable energy resources. Particularly, great attentions are being focused to use biomass as energy feedstock. This is mainly due to the fact that biomass is the most abundant renewable carbon resources in earth [1]. Moreover, it is the second largest source of energy after fossil fuels (oil, coal and natural gas) which provides 80% of the energy derived from renewable sources [2]. Through biological and thermochemical conversions, all forms of energy, *i.e.* biofuels (liquid, gas or solid); heat; electricity, can be generated from biomass [3]. Therefore, biomass is the most versatile renewable energies resource and regarded as the promising alternative feedstock to substitute fossil fuels in energy production.

Extensive bioenergy production requires a large sustainable supply of diverse biomass feedstocks. It is considered because the current development of existing terrestrial-based energy crops faces main issues on land's availability as well as productivity [4]. Land is known to have multiple functions, *e.g.* for the production of food, feed, fiber, materials; human living place; nature conservation; climate protection [2], and these functions are closely linked each others. In addition, land usage for agriculture of energy dedicated crops may intensify the pressure on freshwater resources as well [5]. As such, increased used of land-based biomass for energy production would have multi-dimension impacts.

Marine macroalgae (seaweeds) have been regarded as one of potential alternative resources to supplement terrestrial biomass in energy production [6]. Mainly, it is related with their high carbohydrate content (Table 1) [7], rapid growth rate (3.3-11.3 kg wet weight m^{-2} $year^{-1}$) [8] and high photosynthetic efficiency (6-8%) [6] which show the high productivity of macroalgae. Particularly, their high moisture and low lignin content (70-90% and <10%, respectively [7, 9, 10]) provide advantageous characteristics for biological conversion into alcohols or gaseous fuels. Several studies have reported that these marine biomass could be converted into hydrogen [11], methane [12], ethanol [13], n-butanol [14] and 2,3-butanadiol [15]. Furthermore, the utilization of macroalgae offers potential advantageous than terrestrial-based energy crops. Since they are grown in sea water, their biomass cultivation would not meet with the issues of arable land and freshwater resources. The easy to be harvested make the cultivation process of macroalgae to be economically attractive as well. In fact, 71% earth's surface is covered by sea [16], implying the great opportunity of marine biomass on providing sustainable biofuels.

Table 1. The proximate analysis of some macroalgae

Biomass		**Proteins**	**Lipids**	**Carbohydrates**	**Ash**	**Sources**
		(%-dry weight)				
Brown macroalgae	*Macrocystis* sp.	17	-	37	41	[6, 9]
	Laminaria sp.	3-20	2-3	38-61	15-26	[6, 9, 17]
	Sargassum sp.	17	1	45-50	23	[18]
	Fucus sp.	1-17	<1-3	62-66	19-30	[17]
Red macroalgae	*Gracillaria* sp.	11-20	<1	36-63	25-40	[9, 18]
	Osmundea sp.	24	<1	32	31	[18]
Green macroalgae	*Ulva* sp.	4-14	<1-2	15-65	11-26	[9, 17, 19]
	Codium sp.	19	4	33	36	[18]

Nevertheless, the industrial development of macroalgae for energy is still limited to date. Mainly, it is because their cost over profit is still not economically viable compared with the current low oil price and conventional energy crops. For instances, bioethanol production cost from kelp was analysed to be three times much higher than that from corn ($0.50/kg and $0.16/kg, respectively) [20] due to its low efficiency result than the theoretical value (<40% ethanol yield) [21]. The energy returns on investment (EROI) of biogas production from macroalgae were also reported to be lower than the EROI of conventional biogas [20]. The complex characteristics of macroalgae components, *e.g.* unique chemical structure with sulphated group; mixed sugars; low C:N ratio, are contributed to the ineffectiveness of their biological conversion by using conventional technology [21]. In fact, fresh macroalgae biomass itself has a high price for food and cosmetic industries, which lead them to be economically unfeasible feedstock to be used for generating fuel as a single product due to the low-value of fuel [22]. As the results, additional revenue is required to cover this production cost. Herein, integrating their production with a higher value product (biorefinery) should be considered to provide an additional financial incentive and thus, making their energy production to be more attractive as well as economically feasible.

Macroalgae have been commercially used as a food and/or for the production of their polysaccharides (*e.g.* carrageenans, alginates, agars) [23], which account for 83-90% of their global market value [21]. Nevertheless, they are also known to possess diverse primary or secondary metabolites with great potential applications in pharmaceutical, nutraceutical, and cosmetical industries. Identifying a core group of these compounds and their potential markets are necessary for biorefinery development of macroalgae. Therefore, this review evaluated the potential high-value products that can be derived from macroalgae. The basic information on the biology of macroalgae is presented at first. The current states and the challenges on biorefinery research of macroalgae are discussed as well.

2. Marine macroalgae: biology and ecology

Macroalgae are a diverse group of multicelular, photosynthetic and eukaryotic organisms with lacking true roots, stems and leaves [24]. Approximately, there are 10,000 macroalgal species that are lived in marine habitat [25]. Their distribution and morphological features are mainly depended on the environmental conditions such as substrate, temperature, light quality, dynamic tidal activity, salinity, pH, nutrients and pollution level. Among these conditions, light has significant contributor because of the light absorption selectivity of their respective pigment [26]. Macroalgae have important role in coastal ecosystem. They serve as the primary food producer in the sea. Moreover, they produce oxygen and provide a shelter for marine coastal organisms.

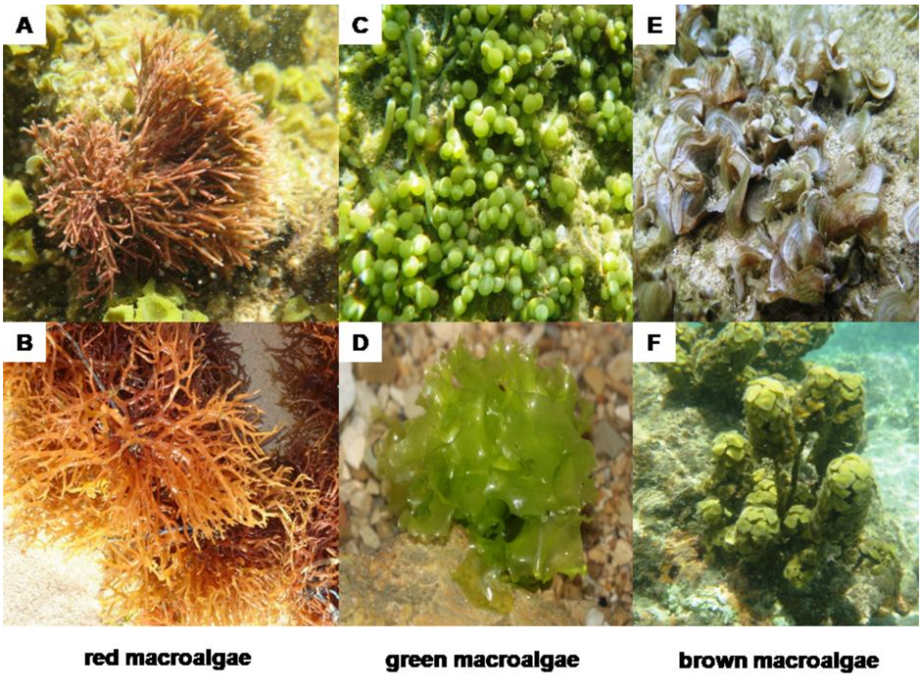

Figure 1. Various species of macroalgae from Indonesian sea water. *Galaxaura rugosa* (A), *Eucheuma cottonii* (B), *Caulerpa racemosa* (C), *Ulva lactuca* (D), *Padina australis* (E), *Turbinaria decurrens* (F).

The reproduction system of macroalgae can occur via sexual and sexual process. In a sexual reproduction, carpogonia from female gametophytes is fertilized by spermatia from male gametophytes. Meanwhile, asexual reproduction is occurred through vegetative fragmentation.

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In general, macroalgae are classified based on their pigments which are green (Chlorophyta), brown (Ocrophyta) and red (Rhodophyta) (Figure 1). The highest diversity is reported to be red macroalgae with more than 7000 species, fsollowed by brown and green macroalgae with 2030 and 600 species, respectively [24]. In addition, they can also be classified based on the types of their carbohydrates, *e.g*. carrageenophytes, agarophytes and alginophytes are groups of macroalgae contained large amount of carrageenan, agar and alginate, respectively.

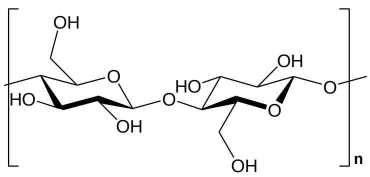
3. High-value chemicals from macroalgae

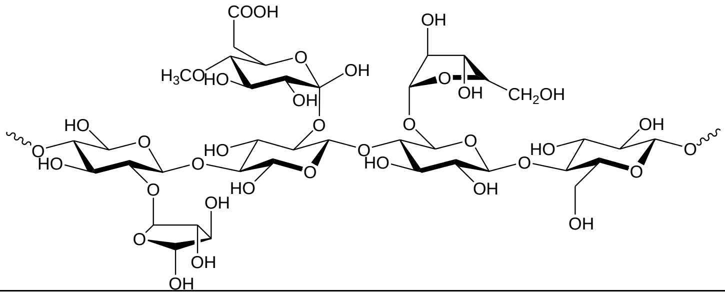
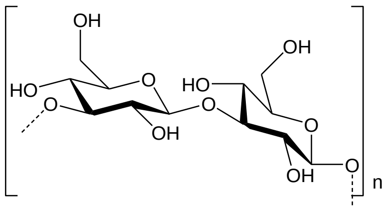
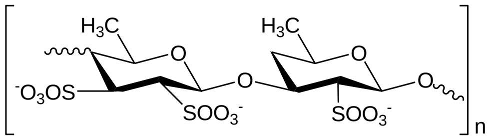
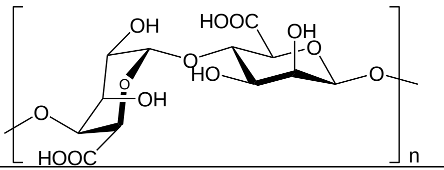
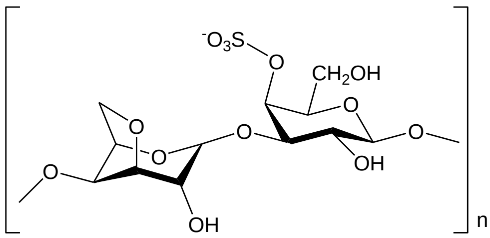
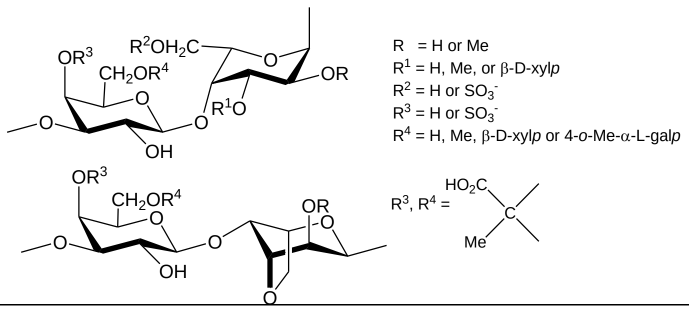
Similar as other living organisms, macroalgae synthesized primary as well as secondary metabolites to support their lives. However, marine habitat has complex conditions, *e.g.* high salinity; wide temperature differences; large nutrient dynamics; and strong UV sunlight exposure. These lead marine organisms like macroalgae to synthesize metabolites with specific chemical as well as physical properties for their survival in such kinds of extreme condition. In spite of their own biological functionality (*e.g.* growth energy, chemical defence), the uniqueness chemical components of macroalgae offer potential application in the production of valuable products with high-economic value and/or market demand. In this section, some potential chemical substances in macroalgae besides for energy and current dietary fiber applications are discussed and presented.

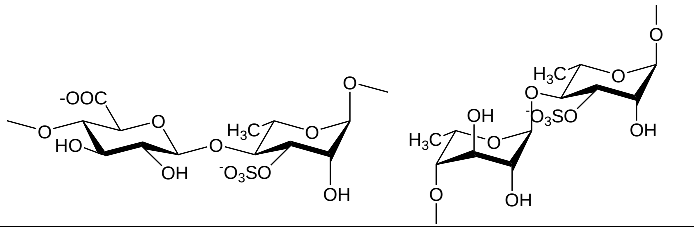
Sulphated oligosaccharides

As a typical photosynthetic organism, macroalgae convert solar energy into chemical energy, particularly, in form of carbohydrates (poly- and monosaccharides). However, the complexities of marine habitat lead their metabolism to synthesize carbohydrates with different chemical characteristics compared with that from terrestrial plants (Table 2). For instances, the major carbohydrate component of all terrestrial plants are cellulose (35-50%) and hemicelluloses (20-35%) [1], which are composed of simple sugars like glucose, xylose, mannose, ribose, arabinose and galactose [27]. Meanwhile, macroalgae have diverse types of carbohydrates with different monomeric sugars (Table 2). As an example, laminaran, fucoidan, alginate are the major polysaccharides that are isolated from brown macroalgae, while galactans (*e.g.* carrageenan and agar) and ulvan are mostly found in red and green macroalgae, respectively.

Table 2. Comparative chemical structure and monomer of some polysaccharides

Biomass	Polysaccharides	Chemical Structure	Monomer
Terrestrial Plants	Cellulose		Glucose

	Hemicellulose		Xylose, arabinose, glucose, mannose, galactose
Brown macroalgae	Laminarin		glucose
	Fucoidan		Sulphated L-fucose
	Alginate		□-D-mannuronic acid, α-L-guluronic acid
Red macroalgae	κ-carrageenan		Sulphate esters of D-galactose, sulphate esters of (3,6)-anhydro-D-galactose
	Agar		Ester sulphate of D-galactose and 3,6-anhydro-L-galactose

Green macroalgae	Ulvan		L-rhamnose, D-xylose, D-glucose, D-glucuronic acid

Among of them, polysaccharides with sulphated groups have received much attention due to their high economic value in food, pharmaceutical and nutraceutical industries. Carrageenan, agar and fucoidan are several macroalgal sulphated polysaccharides that have been largely commercialized. The important application of these sulphated polysaccharides is related with their water-solubility that can give gelling properties into water. Currently, ulvan has also attracted much attention due to their potential medicinal values [28].

Recently, sulphated oligosaccharide derived from macroalgae have attracted much attention because of their biological activities against pathogen bacteria [29]. They can be produced by partially hydrolyzed their respective polysaccharide either by chemical treatment using acid catalyst or enzymatic process. For examples, oligo-ulvans having a molecular weight of 50 to 60 kDa was reported to induce pheylalanine ammonia lyase enzyme, indicating its potential function as antiviral, antifungal and antibacterial activities [29]. Oligo-fucans (10 kDa) obtained by enzymatic hydrolysis of fucoidan showed antiviral activity as well.

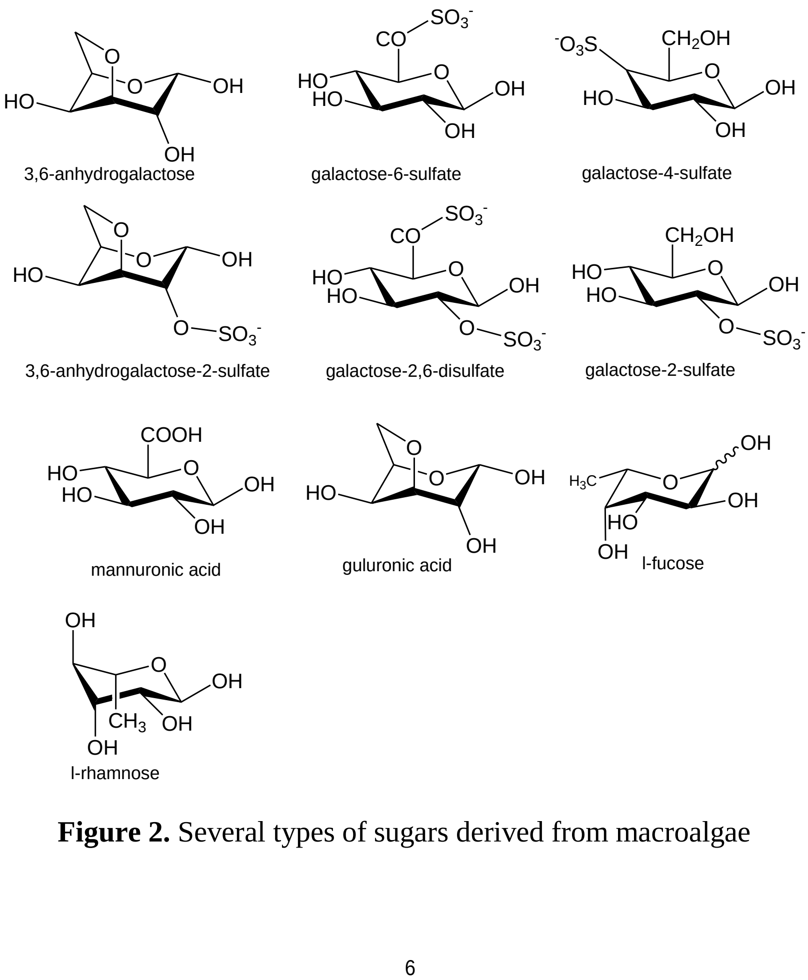


Figure 2. Several types of sugars derived from macroalgae

Rare sugars

Rare sugars are defined as monosacharides and their derivatives that rarely exist in nature [30]. In this classification, all types of sugars besides the seven current abundant sugars, *i.e.* D-glucose; D-galactose; D-mannose; D-fructose; D-xylose; D-ribose; L-arabinose [31, 32], could be categorized as rare. These sugars could be in the form of simple monosaccharides (*e.g.* D-talose; D-lyxose) [33], deoxygenated monosaccharides [31, 34, 35] and sugar alcohols [30, 36]. Despite their low natural abundance, rare sugars have high-market values in pharmaceuticals and nutraceuticals industries due to their wide potential biological activities [31] and low-caloric properties (1-2 kcal g^{-1}) [37]. More recently, rare sugars could act as building block chemicals which attract the study on searching their potential resources and/or developing their efficient catalytic synthesis method [31-33].

Macroalgae are great sources of rare sugars because their polysaccharides are generally composed different types of sugars with unique chemical structure (Figure 2). For instances, fucoidan, which is a heteropolysaccharides isolated from brown macroalgae, contain L-fucose as its main building block. L-fucose is one of rare sugars which has practical application for skin cell generation. Meanwhile, rare sugars like L-rhamnose and glucuronic acid can be found in ulvan isolated from green macroalgae *Ulva* sp. with the content of (17-45%) and (7-19%) [38, 39]. Due to the variety of macroalgae polysaccharides and their unique monomeric sugars, great attentions are being focused on their catalytic synthesis reaction recently [40].

Brown macroalgae contain mannitol in the yield of 10-30% [23, 37], in which, *Laminaria* sp. And *Saccharina* sp. are two main sources [24]. Mannitol is a type of six-carbon sugar alcohol with high-market value (US$7.3 kg^{-1}; global market, 13.6 million kg $year^{-1}$) [37]. It is widely used in the food, pharmaceutical, medical and chemical industries [41]. It is industrially produced by hydrogenation of fructose/glucose mixture (1:1), sucrose or fructose at 120-160^{o}C with Raney nickel as a catalyst with the yield of 17% w/w, 31% w/w and 48-50% w/w, respectively [37]. Due to its large market demand, great efforts are focused to find the effective synthetic method or alternative resources for sustainable production of mannitol.

Proteins and Amino acids

Protein is the second largest primary metabolites in macroalgae. Generally, red macroalgae have the highest protein content (7-47% dw), followed by green and brown macroalgae with the content of 3-30%dw and 10-30%dw, respectively [42]. Among of red macroalgae, *Porphyra* sp. and *Palmaria palmate* are two main sources of protein with the yield of 47% and 35%dw [24]. Meanwhile, *Undaria pinnatifida* (Wakame) and *Ulva* sp. are reported to be the higher protein producer in brown and green macroalgae, respectively with contained of 11-24% and 20-26%, respectively. Interestingly, the proportion of high-value proteins containing essential amino acids in macroalgae proteins is relatively high (38-40%) [42]. The amino acid composition of macroalgae proteins is mainly aspartic, glutamic acid, valine, leucine and lysine [24].

Pigment

As typical photosynthetic organism, macroalgae have pigment molecules to absorb light. Three major classes of these molecules are chlorophylls, carotenoids (carotenes and xantophylls) and phycobiliproteins, which are responsible to give the colour appearances of green, brown and red, respectively. Herein, chlorophills have main role on photosynthesis and is a major pigment in most macroalgae [42]. Meanwhile, the two later pigments have activity for photo-absorption at low light intensities and photo-protection from excess light [24]. As such, these pigments have potential applications as natural colorant and for UV protector as well as anti oxidizing agent.

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The pigment content in macroalgae is varied depended on the species and growth habitat. The chlorophyll a content of green, brown and red macroalgae are reported to be 0.4-34.5, <1-10.5 and <1-9.8 mg/g dw, respectively [42]. The carotenoids of brown, green and red macroalgae are about 0.2-2.7, 0.1-0.4 and <1-1.8 mg/g dw, respectively, in which, fucoxanthin is the major carotenoids of brown macroalgae (0.1-2.7 mg/g dw). Meanwhile, phycobiliprotein is only present in red macroalgae in the range of <1-125 mg/g dw. Since chlorophylls and carotenoids are liposoluble molecules, they are commonly extracted by using organic solvents such as acetone, methanol or dimethyl sulfoxide (DMSO) [42]. Meanwhile, due to its high solubility in water, phycobiliproteins can be extracted by water or buffers.

Fucoxanthin is one of compounds in carotenoid groups that attract much attention currently due to their potential medical and nutraceutical applications. It contributes 10% of carotenoids in nature [43]. Focoxanthine and its derivatives have been reported to have some biological activities like antiobesity, antitumor, antioxidant, anti-inflammatory and hepatoprotective activities [44]. Meanwhile, phycoerythrin is a valuable pigment in phycobiliprotein groups. It can be significantly found in red macroalgae. Beside as a colorant, it has potential application as fluorescent probe [45].

Phenolic compounds

Macroalgae live in marine habitat that has strong UV exposure. To protect from photo-destruction, their metabolism synthesized phenolic compounds that exhibit free-radical scavenging properties. Among of them, brown macroalgae has the highest contain of polyphenols which are called phlorotannins [24]. Many reports showed that phlorotannins have antioxidant potential in cancer chemoprevention [46].

4. Current states and challenges

Several reports have been conducted in order to get the feasibility of the integration of biofuel production with other valuable products from macroalgae. Baghel *et al*. initially reported the integration of bioethanol production and multiple commodity chemicals derived from red macroalgae *Gellidella acerosa* and *Gracilaria dura*. Herein, fermentation for biofuel production was conducted in the final step after extracting the valuable chemical components contained in the sample of macroalgae (Figure 3). In the scale of 0.05-0.5 kg of raw material, this integration process had advantages compared with single production process, *e.g.* gel strength improvement of the obtained agar (1.5-3 folds); low residue; chemical usage reduction up to 85% [47]. In addition, sequence extraction of valuable chemicals from green macroalgae *Ulva fasciata*, *i.e.* minerals; lipid; ulvan; cellulose, and fermentation of its cellulose into ethanol was also reported to give similar products yield and purity as individual extractions [48]. Although computational analysis of 1 tone scales was reported to have realistic results, there is still lack information on their large-scale experimental results.

The great interest of macroalgae is related with their potency as a feedstock for the production of rare sugars. Although these sugars can be found as a free monosaccharide in some macroalgae, they are commonly observed as a polymer. As such, the development of the catalysis processes for hydrolysis of macroalgae polysaccharide is one of current issues in marine-based biorerinery. Particularly, designing the solid acid catalyst is required in order to get the effective results with several advantages in the scope of green chemistry (reusable, stable and recyclable). It is driven with the fact that each types of these catalysts show different catalytic activity when using polysaccharides from macroalgae compared with that from terrestrial biomass (*e.g.* starch) [40].

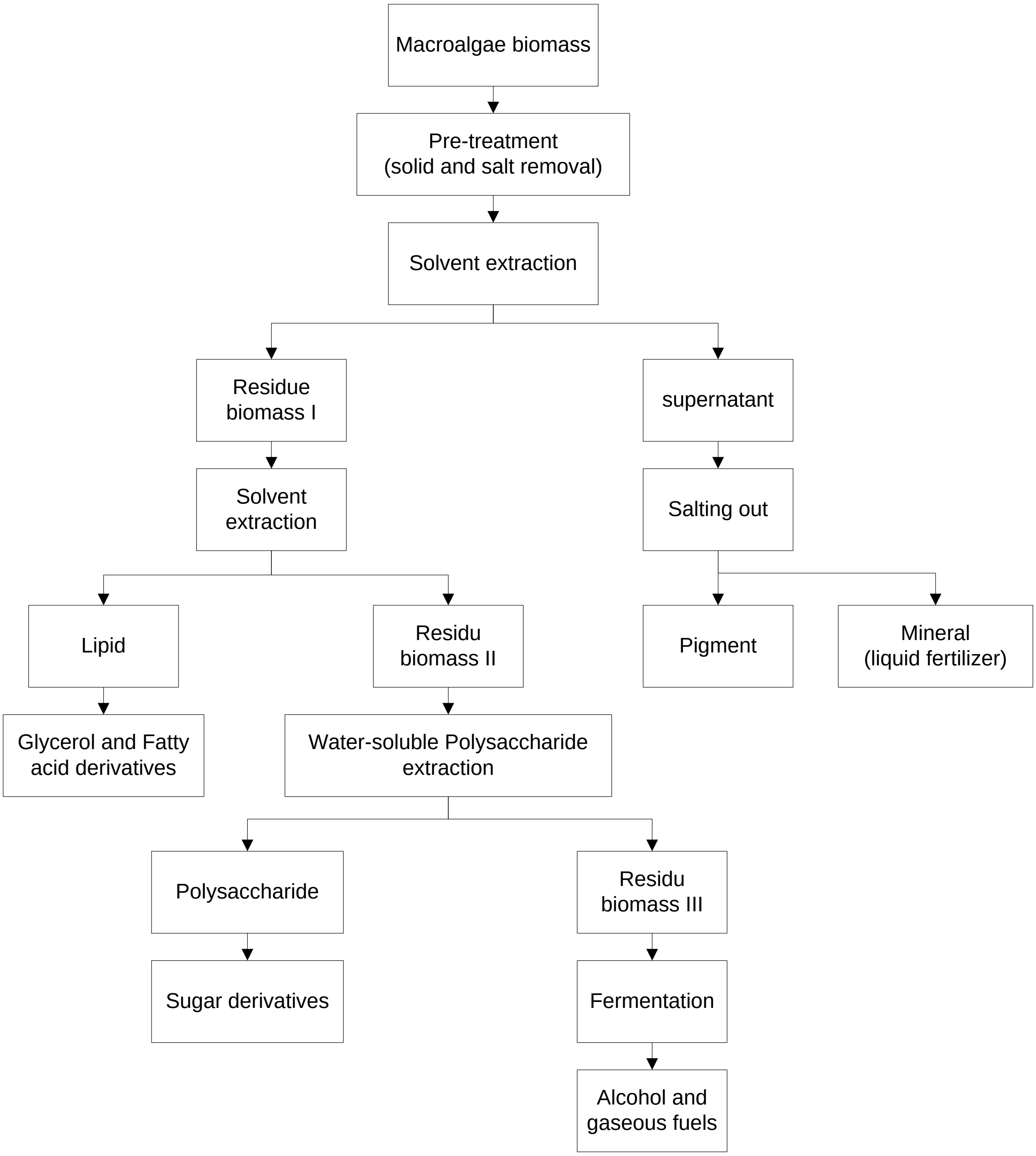

Figure 3. Schematic diagram of the production of biofuel and valuable products from macroalgae.

Polysaccharides of macroalgae could be also catalytically converted to generate other valuable platform chemicals, especially with the application in energy. By using acid catalysts, they could be dehydrated into 5-hydroxymethylfurfural (HMF) which is one of top-value added chemicals in the sugar-based refinery. Moreover, further catalytic reaction could generate levulinates which have wide range applications in industry such as fuel additives, fragrances, solvents, plasticizers and green pesticides [49, 50]. The recent research showed that these two platform chemicals were found during acidic hydrolysis reaction of carrageenan into 3,6-anhydrogalactose [51]. The chemo-catalytic processes offer several advantages than biological fermentation such as faster reaction rates, wide range of the sugar types and simpler protocols which makes the utilization of macroalgae especially for energy to be more efficient and attractive.

The unique polysaccharides of macroalgae also offer the great opportunity in the field of material synthesis with wide potential application in industry. For instances, the presence of sulphated functional group of macroalgae polysaccharide can be used to obtain sulphonic acid material that have potency for catalysis reaction over acid catalyst. Moreover, it can be used to prepare nanoparticle which can give material with antimicrobial properties. In current report, macroalgae can be a potential renewable source for porous materials [52]. These materials currently have great attentions due to the potential application in the field of separation process and catalyst support.

As discussed above, chemical components of macroalgae is affected by their growth habitat environmental condition and seasons. For example, the content of rhamnose in *Ulva* sp. could vary in the range of 17-23% in the period June-September due to the different nutrient dynamics in this period. Meanwhile, mannitol in *Laminaria digitata* is reported to vary in the value of 5-32% [53]. The different nitrogen contents of macroalgae biomass that are harvested in November-May and July-October were also reported, which could indicate the seasonal variation of their protein content [54]. Therefore, controlling the large-scale cultivation of macroalgae to get standardized product could be very challenges considering of the complexity of marine habitat.

5. Conclussions

Marine macroalgae live in the habitat with complex conditions such as high salinity, wide temperature differences, large nutrient dynamics, and strong UV sunlight exposure. These extreme conditions lead their metabolism to synthesize primary as well as secondary metabolites with unique chemical structure for their survival. As a typical photosynthetic organism, macroalgae convert solar energy into chemical energy, especially in form of carbohydrates. Their high carbohydrate content leads them to have potency as a renewable feedstock for alcohol or gaseous fuels. In addition, the uniqueness their chemical structure offers a great opportunity to produce variety of carbohydrate-based chemicals that has potential market in pharmaceutical as well as nutraceuticals industries such as sulphated oligosaccharides and rare sugars. More interestingly, it offers potential application in material synthesis with novel physicochemical properties. Macroalgae also contain several kinds of valuable products like essential amino acids, pigments and polyphenols. Integrating the production of bioenergy and valuable chemicals could make the bioenergy development from macroalgae to be more economically attractive as it gives potential additional revenue, high efficiency as well as more environmentally results.

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