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## Review

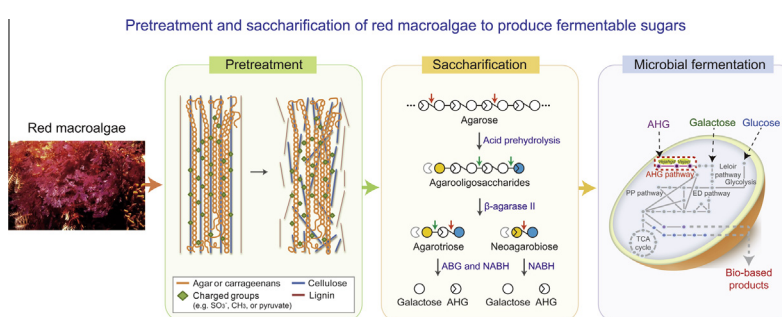
## Pretreatment and saccharification of red macroalgae to produce fermentable sugars

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## HIGHLIGHTS

- The major polysaccharides of red macroalgae are agar and carrageenans.
- Pretreatment of red macroalgae increases the substrate accessibility to enzyme.
- Chemical prehydrolysis and enzymatic saccharification provide sugars from agar.
- Agarolytic  $\beta$ -galactosidase is the key enzyme for the complete monomerization of agar.
- The novel catabolic pathway of 3,6-anhydro-L-galactose is recently discovered.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Red macroalgae are currently considered as renewable resources owing to their high carbohydrate and low lignin and hemicellulose contents. However, utilization of red macroalgae has been limited owing to the lack of established methods for pretreatment and an effective saccharification system. Furthermore, marine red macroalgae consist of the non-favorable mixed sugars for industrial microorganisms. In this review, we suggest strategies for converting red macroalgae to bio-based products, focusing on the pretreatment and saccharification of red macroalgae to produce fermentable sugars and the microbial fermentation of these sugars by industrial microorganisms. In particular, some recent breakthroughs for the efficient utilization of red macroalgae include the discovery of key enzymes for the complete monomerization of red macroalgal carbohydrate and the catabolic pathway of 3,6-anhydro-L-galactose, the most abundant sugar in red macroalgae. This review provides a comprehensive perspective for the efficient utilization of red macroalgae as sustainable resources to produce bio-based products.

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## 1. Red macroalgae as renewable biomass

## 1.1. Marine macroalgae as third-generation biomass

Currently, the utilization of renewable resources is essential to achieve sustainable fuel production to solve the problem of

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excessive production of greenhouse gases that cause global warming (Alonso et al., 2010; Goh and Lee, 2010; Subhadra and Edwards, 2010). In this context, bioethanol production using corn and sugarcane (Bothast and Schlicher, 2005; Cardona et al., 2010) and biodiesel production using soy bean and sunflower (Wesseler, 2007) are considered feasible strategies for industrialization since they are based on mature technologies. However, the use of edible crops for biofuel production can cause competition between food and fuel production. Alternatively, lignocellulosic biomass such as wood wastes, agricultural residues, and energy crops, which are considered second-generation biomass (Alonso et al., 2010; Limayem and Ricke, 2012), is an attractive option for biofuel production owing to the lack of direct competition with other food resources. However, the competition for arable land between edible crops and lignocellulose and the high cost of breaking the natural recalcitrance of lignocellulose can be obstacles for the utilization of lignocellulosic biomass (Öhgren et al., 2007; Yang and Wyman, 2004).

To overcome the problems caused by using edible crops and lignocellulosic biomass, marine macroalgae have recently received much attention as third-generation biomass. There are many advantages of using marine macroalgae, such as their higher carbohydrate content, lower amounts of recalcitrant substrates such as lignin, no competition with food production, and no requirements of arable land and fertilizer for growth (Goh and Lee, 2010; Kim et al., 2011; Park et al., 2012; Subhadra and Edwards, 2010). In this review, we will focus on the potential of marine red macroalgae as an alternative renewable biomass.

### 1.2. Carbohydrate compositions of red macroalgae

The carbohydrate compositions of marine macroalgae largely differ from those of terrestrial plants, which are mainly composed of cellulose and hemicellulose (Sun and Cheng, 2002). The carbohydrate compositions of marine macroalgae highly depend on the species of macroalgae (Park et al., 2012; Roesijadi et al., 2010; Wargacki et al., 2012; Wei et al., 2013). Red macroalgae (*Rhodophyta*) are classified into agarophytes and carrageenophytes based on the presence of major carbohydrates, agar and carrageenans, respectively.

The main carbohydrate of agarophytes, agar, is composed of neutral agarose as the major component and charged agaropectin as the minor component (Duckworth and Yaphe, 1971). Agarose is a heteropolysaccharide composed of equal molar amounts of D-galactose and 3,6-anhydro-L-galactose (AHG). AHG is linked to D-galactose via  $\alpha$ -1,3-glycosidic linkages, and the resulting heterodimers (i.e.,  $\alpha$ -neoagarobiose; 3,6-anhydro-L-galactosyl- $\alpha$ -1,3-D-galactose) are linked to form agarose polysaccharides via  $\beta$ -1,4-glycosidic bonds. Agaropectin is a polysaccharide consisting of alternating units of D-galactose and AHG, which are highly substituted by ester-sulfates, methyl groups, or pyruvates (Delattre et al., 2011; Qi et al., 2008). Owing to the structural complexity of agaropectin, its chemical structure has not been fully identified to date.

The ratio of agarose and agaropectin varies depending on the agarophyte genus, origin, and harvesting season (Lemus et al., 1991). For example, the agarose content in agar is much higher in the species of *Gelidium* and *Pterocladia* than that of *Gracilaria* species (Hehemann et al., 2012a; Lemus et al., 1991; Park et al., 2012). The amount of agarose in agar determines the quality of agar, such as the gel strength and gelling temperature (Duckworth and Yaphe, 1971).

Carrageenans, the major carbohydrates in carrageenophytes, are sulfated polygalactans composed of D-galactose and 3,6-anhydro-D-galactose with variable ester-sulfate contents (15–40%, w/w) (Necas and Bartosikova, 2013). The two monomeric

units are joined by  $\beta$ -1,4- and  $\alpha$ -1,3-glycosidic linkages. Carrageenans are classified as  $\kappa$ ,  $\iota$ , and  $\lambda$  types based on their solubility in potassium chloride and their gel-forming ability. The primary differences that influence the properties of carrageenan types are determined by the contents of ester-sulfates and 3,6-anhydro-D-galactose (Necas and Bartosikova, 2013). Among the three types of carrageenans,  $\kappa$ -carrageenan, which forms a strong and rigid gel in the presence of potassium ions, contains the lowest content of ester-sulfates (25–30%, w/w) and the highest content of 3,6-anhydro-D-galactose (28–35%, w/w) (Barbeyron et al., 2000). By contrast,  $\lambda$ -carrageenan, which does not have gelling ability, contains the highest content of ester-sulfates (32–39%, w/w) but does not contain 3,6-anhydro-D-galactose (Barbeyron et al., 2000). The  $\kappa$ ,  $\iota$ , and  $\lambda$  types of carrageenans are mainly produced from the species of *Chondrus*, *Gigartina*, and *Solieria*, respectively (Chen et al., 1973).

Cellulose, a polysaccharide consisting of a linear chain of  $\beta$ -1,4-linked D-glucose units, is the minor component of red macroalgae [ $\sim$ 15 wt% of dry biomass of red macroalgae (Park et al., 2012)].

### 1.3. Advantages of using red macroalgae over other marine macroalgae

Brown and red macroalgae have been more actively produced and utilized than green macroalgae. This is mainly because the top five genera belonging to brown and red macroalgae, *Laminaria*, *Undaria*, *Porphyra*, *Eucheuma*, and *Gracilaria*, comprise 76% of the total amount of macroalgae production (Roesijadi et al., 2010). The carbohydrate compositions of brown macroalgae are more complex than those of red macroalgae. Alginate, laminarin, fucoidan, and cellulose are the major polysaccharides (Wargacki et al., 2012; Wei et al., 2013). D-Mannuronate and L-guluronate are produced by the acid hydrolysis of alginate, whereas 4-deoxy-L-erythro-5-hexoseulose (DEH) is enzymatically produced by alginate lyase. The microbial platform for producing ethanol using brown macroalgal carbohydrates was enabled by introducing the ethanol pathway into the alginate-assimilating microorganism *Sphingomonas* sp. A1 (Takeda et al., 2011) or by introducing the alginate pathway into *Escherichia coli* (Wargacki et al., 2012). Recently, the microbial platform for ethanol production from brown macroalgal carbohydrates was further enhanced by using the recently discovered DEH transporter from the alginateolytic eukaryote *Asteromyces cruciatus* (Enquist-Newman et al., 2014; Schaumann and Weide, 1995).

Unfortunately, the monomeric sugar yields of brown macroalgae ( $\sim$ 27 wt% of total dry biomass) were significantly lower than those of red macroalgae ( $\sim$ 53 wt% of dry biomass) due to the lower carbohydrate content and the inefficient saccharification method of brown macroalgal carbohydrates (Jang et al., 2012; Kim et al., 2011; Yoon et al., 2010). In addition, the carbohydrate compositions of brown macroalgae are more complex than those of red macroalgae since red macroalgae are composed of galactose-based polysaccharides (i.e., agar and carrageenans) and glucose-based cellulose. The total carbohydrate contents of red macroalgae ( $\sim$ 79 wt% of dry biomass) are much higher than those of brown ( $\sim$ 50 wt% of dry biomass) and green macroalgae ( $\sim$ 60 wt% of dry biomass) (Jang et al., 2012; Kim et al., 2011; Yoon et al., 2010). Taken together, these findings demonstrated that red macroalgae have advantages over other macroalgae with respect to saccharification and fermentation.

## 2. Pretreatment of red macroalgae

To enhance the saccharification of red macroalgae carbohydrates, pretreatment of red macroalgae is essentially required by

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