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Review

Sustainable production of bioethanol from renewable brown algae biomass

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ABSTRACT

Brown algae have been considered as renewable biomass for bioethanol production because of high growth rate and sugar level. Saccharification of brown algae biomass is relatively easy due to the absence of lignin. Among the major sugar components of brown algae, alginate cannot be directly used because industrial microorganisms are not able to metabolize alginate. This problem has been overcome by the development of metabolically engineered microbes to efficiently utilize alginate. This review analyzes and evaluates recent research activities related to bioethanol production from brown algae. This review mainly deals with the recent development and potential of a metabolically engineered microbial cell factory and bioethanol production from brown algae biomass including alginate as the main carbohydrate. Future researches for cost-effective bioethanol production from brown algae are discussed.

Contents

1. Introduction

Due to the decline of petroleum reserves and a dramatic explosion in demand for energy, various types of alternative energy have been extensively investigated. Biofuel such as bioethanol, biodiesel and biohydrogen is one of the promising alternatives [1–3]. However, the production of biofuels from biomass has some drawbacks. In the case of first-generation biomass, there are moral issues with using food for biofuel production. In order to use second-generation lignocellulosic biomass, cost-intensive pretreatment is absolutely required before saccharification and fermentation [4].

Macro- and microalgae are an example of third-generation biomass [5]. Algae present several advantages over other types of biomass. Algae are the fastest growing photosynthetic organisms [6]. Algae can efficiently remove carbon dioxide and synthesize polysaccharides or oil that can be used for biofuel production [7]. Generally, algal carbohydrates can be used for bioethanol fermentation after relatively easy saccharification due to the absence of lignin [5]. Oil can be trans-esterified into biodiesel [8]. In addition, algal biomass can be directly used for heat and power generation using anaerobic digestion and pyrolysis [9–11] (Fig. 1).

There are three types of macroalgae, brown, green and red algae [12]. Brown algae such as sea mustard (*Undaria pinnatifida*) and kelp (*Saccharina japonica*) are one of the promising biomass for biofuel production because cultivation productivity based on area is the highest among three types of macroalgae [13,14],

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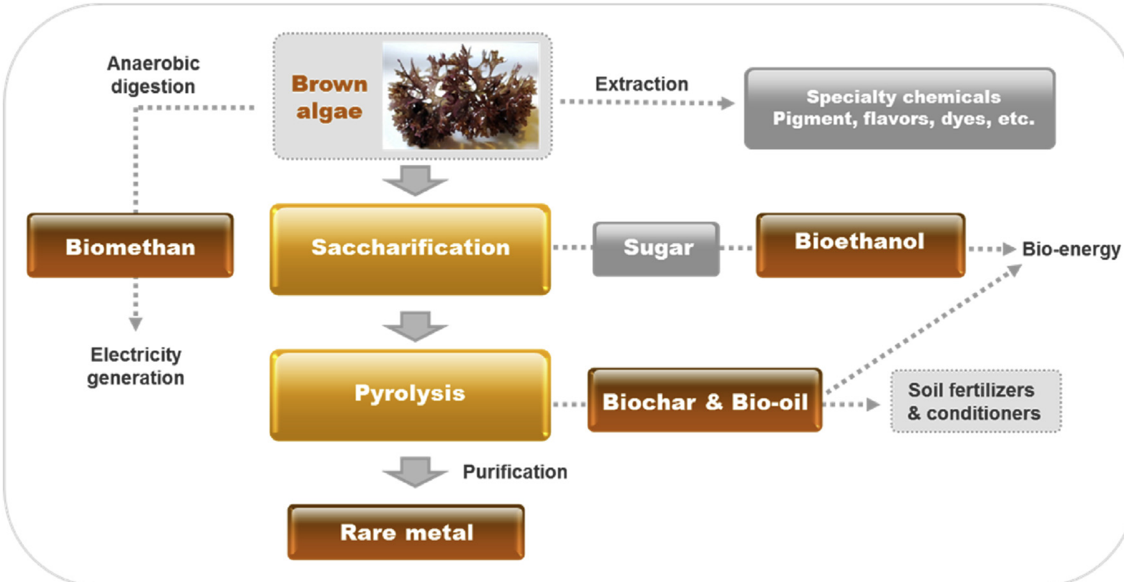

Fig. 1. Conceptual diagram of brown algae for production of biofuels and biochemicals.

approximately 40 kg wet biomass/m^2 of gulf-weed (*Sargassum muticum*), compared to 2.3 and 6.6 kg/m^2 of green laver (*Ulva lactuca*) and agar weed (*Gelidium amansii*), respectively. The large-scale cultivation of brown algae is already practiced in several countries including Korea, China and Japan. Compared to microalgae, brown algae have a higher sugar and lower oil contents. Thus, brown algae are a more suitable feedstock for bioethanol production than biodiesel. With respect to bioethanol productivity, one report prepared for the US Department of Energy claimed that bioethanol productivity from macroalgae per hectare per year could theoretically be two times higher than sugarcane and five times higher than corn [15]. This review is intended to analyze and evaluate recent research activities related to biofuel production from brown algae, especially bioethanol. This review mainly deals with the recent development and potential of a metabolically engineered microbial cell factory and bioethanol production from brown algae biomass including alginate as the main carbohydrate.

2. Brown algae as renewable and sustainable biomass

Brown algae have several advantages as a feedstock for production of biofuels. Firstly, brown algae avoid competition with food production. Brown algae requires no arable land and are cultivated in the ocean using aquaculture without needing the expensive nutrients, fertilizers or fresh water that are required for conventional agriculture. Brown algae have no lignin, and thereby no extensive pretreatment is used to release sugars, but just using simple operations such as milling or crushing. There is no moral issue associated with the use of brown algae for biofuel production. One particularly important advantage is that brown algae can offer high biomass yields per acre [13,14]. Brown algae contain high levels of carbohydrates, contributing up to 55% (w/w) of the dry biomass [16]. Therefore, brown algae are an ideal renewable and sustainable biomass due to its abundance and high sugar levels that can be used for production of bioethanol and chemicals.

Roughly 70 million dry tons of macroalgae are cultivated and harvested worldwide in offshore and near-shore coastal farms [17]. This production scale is mostly for food applications. Cultured brown algae are harvested by both manual and mechanical methods. The harvested brown algae are then normally treated with milling to reduce biomass sizes for efficient saccharification or alginate extraction [18] (Fig. 2). The saccharified broth can be used for bioethanol fermentation.

3. Bioethanol production from brown algae

The most abundant sugars in brown algae are alginate, mannitol and laminarin. Mannitol and glucose from laminarin (a form of glucan in brown algae) are normal sugars that are efficiently used for bioethanol fermentation [19,20]. Laminarin and mannitol from *Laminaria hyperborea* extracts were fermented to bioethanol under oxygen-limiting conditions using *Zymobacter palmae* [21]. Bioethanol with a yield of 0.4 g ethanol/g of sugars was produced with ethanogenic *Escherichia coli* KO11 from *Laminaria japonica* hydrolysates mainly containing mannitol after chemo-enzymatic saccharification [22]. Ethanol of 7.7 g/L was produced from *S. japonica* biomass using the simultaneous saccharification and fermentation (SSF) method with a theoretical yield of 33.3% [23].

Alginate is a structural polysaccharide in the cell wall of brown algae [24,25]. In some brown algae, alginate constitutes up to 60% of the total sugars. Thereby, alginate, the most abundant carbohydrate, should be utilized for the production of bioethanol. Alginate is present in the insoluble calcium salt form [18]. In the alginate extraction process, calcium alginate is converted to alginic acid in an acid pre-extraction step, and then alginic acid is converted to soluble sodium alginate in alkaline extraction [26]. Alginate can be degraded into unsaturated uronate monosaccharides using alginate lyase [27]. Alginate lyase is the enzyme that catalyzes the β-elimination breakage of the glycosidic bond of alginate. Various alginate lyases have been cloned and characterized [28–30]. Recently, alginate lyase-based saccharification has been developed by employing exolytic alginate lyase as the biocatalyst with a 30% yield [31,32].

Theoretically, ethanol cannot be directly synthesized from unsaturated uronic monosaccharides under anaerobic conditions because no NADH is available for alcohol dehydrogenase to catalyze the conversion of acetaldehyde to ethanol. The NADH generated from glyceraldehyde-3-phosphate (G-3-P) to pyruvate is used for the conversion of 4-deoxy-L-erythro-hexoseulose uronate (DEH) to 2-keto-3-deoxygluconate (KDG) (Fig. 3). As a result, the net NADH