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Bioethanol production from farming non-food macroalgae in Pacific island nations: Chemical constituents, bioethanol yields, and prospective species in the Philippines

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ABSTRACT

Increasing biofuel production on agricultural lands in tropical island nations will likely result in increased deforestation [1], and also inflate food prices, especially in net food importing countries like the Philippines [2–4]. Compounding problems associated with promotion of biofuels in southeast Asian countries are the technical efficiencies of bioethanol production, including poor energy balances from terrestrial crops that are close to, or less than unity, unless bagasse is used as the distillation heat source [1]. As the increase in terrestrial biofuel production in Pacific island nations is potentially less sustainable than is publically stated, alternative feedstocks are required which retain the regional development benefits, while reducing the negative ecological and food security impacts [1,5]. This work presents the potential of farmed macroalgae chemical substrates as a bioethanol feedstock supply, explores macroalgae-to-bioethanol yields, and details prospective non-food macroalgae species, specific to the Philippine coastal region. Leveraging off the existing capability of the macroalgae farming industry (producing 1.7 million wet tonnes annually in the Philippines alone), a significant new market for non-food macroalgae stimulated by bioethanol producers can be developed to avoid problems related to food/feed grade ethanol feedstocks.

Contents

1. Introduction

1.1. The current status of bioethanol demand and production in the Philippines

According to the Philippine's Department of Energy (DOE), the Philippines required around 219 mL of bioethanol in 2010 to comply with the 5% by volume gasoline blending mandate, as per the Biofuel Act of 2006 (RA 9367). The Act's blending rate increased to 10% (by volume) in 2011, which is expected to displace around 461 mL of mineral fuel demand (Table 1). By 2014, the general increase in national fuel consumption is projected to increase bioethanol demand to 536 mL annually [6]. National deforestation and food security risks from the increasing biofuel demand requires judicial industrial development [1–5]. As of 2009, there were only two local bioethanol producers, Leyte Agri Corp, and San Carlos Bioenergy Inc. The Leyte Agri Corp commenced bioethanol

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Table 1
Projected bioethanol demand, based on projected gasoline consumption in the Philippines.

Year	Gasoline demand (mL)	Bioethanol blend required by the Biofuels Act 2006	Fuel displacement (mL)
2006	3,574.96	–	–
2007	3,760.86	–	–
2008	3,956.43	–	–
2009	4,162.16	5%	208.11
2010	4,378.59	5%	218.93
2011	4,606.28	10%	460.63
2014	5,362.87	10%	536.29

Source: [6].

production in late 2008, with an approximate annual production capacity of 9 mL. The San Carlos Bioenergy Inc., the larger facility of the two, commenced operation in late 2009 as an integrated sugar mill, cogeneration plant, and distillery, with an estimated annual bioethanol capacity of 30 mL [7]. In 2011, the Ethanol Producers Association of the Philippines reported that approximately 80 mL will be produced [8]. However, these production figures translate to annual domestic production deficit of 170 mL in 2009 and 140 mL in 2011. Currently, the shortage of domestic bioethanol is met by importing bioethanol from Brazil [7,9]. To redress the domestic deficit, the Philippine Government plans to develop a USD5 million, 100 ha bioethanol macroalgae farm in the province of Aurora in Luzon, using technology developed by the Korean Institute for Industrial Technology [10].

2. Macroalgal biomass as a bioethanol feedstock

Macroalgae are a promising bioethanol feedstock due to their fast growth rate and large biomass yield, with superior productivity to many terrestrial crops [11]. (Table 3 compares macroalgae with conventional terrestrial bioethanol feedstocks, such as sugarcane, corn, and wheat). The high yield of macroalgae is attributed to their lower energy requirement for the production of supporting tissues than terrestrial plants, in addition to their capability to absorb nutrients over their entire surface area [11], and the energy-savings derived from zero requirements for internal nutrient transport [12]. Many types of seaweed exhibit a mass productivity of 13.1 kg dry weight m^{-2} over a seven month growth period, compared to terrestrial plants achieving 0.5–4.4 kg dry weight m^{-2} over an entire year [12–14]. Furthermore, macroalgae generally have a greater hydrolysable carbohydrate content, and potential volume of ethanol than current bioethanol feedstocks [11].

Table 2
Chemical composition of *Ascophyllum nodosum*.

Component	%	Comments
Water	67–82	Decreased with salinity and lowered during the spring
Ash	18–24	Increased from autumn to spring
Alginic acid	24–29	Fluctuates during the year
Laminarin	1.2–6.6	Increased from spring to late autumn
Mannitol	6.8–10.4	Increased from early spring to early autumn
Fucoidan	4–10	
Other carbohydrates	10	
Protein	4.8–9.8	Increased from autumn to spring
Fat	1.9–4.8	Increased from early spring to late autumn
Fibre (cellulose)	3.5–4.6	Almost constant throughout the year
Polyphenols	0.5–14	Lower during spring and increased greatly with salinity

Source: [35].

2.1. Chemical characteristics of macroalgae

Macroalgae are historically divided into three major groups based on their photosynthetic pigments: Chlorophyta (green algae), Rhodophyta (red algae), and Phaeophyta (brown algae) [16,17]. The majority of the pigments in green algae are chlorophylls a and b. The photosynthetic product of green macroalgae is starch, and the outer and inner layers of their cell wall are predominantly pectin and cellulose, respectively [18]. The red macroalgae pigment is r-phycoerythrin, and the cell walls contain small amounts of cellulose, while the majority is gelatinous or amorphous sulfated galactan polymers, such as agar, carageenan, funoran, etc. Brown macroalgae colouration is due to the predominance of xanthophyll pigments, especially fucoxanthin [16]. Brown macroalgae cell walls are composed of alginic acid, cellulose, and other polysaccharides. The food reserves of this group are the carbohydrates laminarin and mannitol, which are particularly suited to ethanol production [19,20].

Macroalgae with high carbohydrate contents are promising candidates for bioethanol production, including: *Sargassum, Gracilaria, Prymnesium parvum*, *Euglena gracilis*, *Gelidium amansii* [12], and *Laminaria* [15]. Macroalgae carbohydrate contents vary widely by species and cultivar, and species selection can develop strains with very high contents of carbohydrate for use as an efficient bioethanol feedstock. Brown macroalgae such as *Laminaria* spp. contain up to 55% (dry weight) of carbohydrates laminarin and mannitol [15,21]. This work focuses on the suitability of the *Sargassum* spp., a brown macroalgae which has relatively high carbohydrate content. (Table 4 shows the results of proximate analyses of two species of Philippine *Sargassum* macroalgae).

The brown macroalgae carbohydrates consist of primarily cellulose, hemicellulose, free sugars, and also the energy storage molecules laminarin and mannitol [19]. As crude fibre is composed of cellulose and hemicelluloses, the % carbohydrates in Table 4 only constitute the storage products and free sugars. However, macroalgae constituents are not constant throughout the year. As an example, research by Horn [21] on the composition of brown algae, *Ascophyllum nodosum* (Table 2), describes seasonal component flux, and also includes indicative magnitudes for each component during the year. The brown algae described in Table 2 are comprised of around 24–29% alginic acid, a polymer of D-mannuronic and L-guluronic acids covalently linked together in sequence. Alginic acid is a common polysaccharide found in the cell walls of brown algae, and in extracted form it quickly absorbs water, making it useful as an additive in dehydrated products, paper and textile manufacture, in addition to use as a food thickener and stabiliser [16]. On a dry weight basis, the amount of alginic acid in brown seaweed is usually between 10% and 25%, which is dependent somewhat on the depth of the seaweed grown in the farm [21]. Therefore, the location, time of year, and the unique habitat all influence alginic acid production, which needs to incorporated in farming design and planning [22].

Laminarin is a storage glucan (a polysaccharide of glucose) found in brown algae and is used as a carbohydrate food reserve. It is a linear polysaccharide made up of β (1,3)-glucan [25]. Mannitol is a low molecular mass sugar alcohol composed of carbon, hydrogen, and multiple hydroxyl groups. In addition to mannitol forming a component of the laminarin molecule, mannitol performs an osmoregulatory role in macroalgae [26]. Glucanases are relatively common, and many microorganisms can hydrolyse laminarin to its glucose monomer, a suitable fermentation substrate. However, mannitol is not readily fermented as many microorganisms are not able to perform strictly anaerobic fermentation of mannitol [21]. Therefore, mannitol must be oxidised to fructose by the enzyme mannitol dehydrogenase to produce the reduced from of nicotanimide adenine dinucleotide (NADH) [21,27].