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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 \cite{1}, and also inflate food prices, especially in net food importing countries like the Philippines \cite{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 \cite{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.

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]. As of 2009, there were only two local bioethanol producers, Leyte Agri Corp, and San Carlos Bioenergy Inc. The Leyte Agri Corp commenced bioethanol 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].

[Insert Table 1 approximately here]

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 4 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].

[Insert Table 2 approximately here]

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, Glacilaria, 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 2 shows the results of proximate analyses of two species of Philippine Sargassum macroalgae).

[Insert Table 3 approximately here]
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 the Table 2 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 3), describes seasonal component flux, and also includes indicative magnitudes for each component during the year. The brown algae described in Table 3 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 form of nicotinamide adenine dinucleotide (NADH) [21,27].

3. Recent macroalgae fermentation techniques and results
Macroalgae are gaining some attention as an alternative renewable source of biomass for the
production of bioethanol, although algal fermentation facilities are relatively expensive to
construct and operate, although are known to be reliable and produce high yields with a range
of feedstocks [28]. Fermentation is usually undertaken using yeasts, although some bacteria
can be utilised. Research by Horn et al. [21] demonstrated the possibility of fermenting
extracts from Laminaria hyporbea (a brown algae) to ethanol using Pichia angophorea (a
yeast) with a maximum yield of 0.43 g ethanol per g of substrate. Further research by Horn et
al. [27] focussed on production of ethanol from synthetic mannitol using the bacterium
Zymobacter palmae under different oxygen regimes. The bacteria successfully grew and
produced bioethanol in the synthetic mannitol medium under oxygen-limiting conditions,
with a yield of 0.38 g ethanol per g of mannitol. In the same work, Horn et al. [27] used
glucose and mannitol as a mixed substrate in combination with an extract from L. hyporbea
to determine the efficacy of the bacteria to ferment mannitol from L. hyporbea extracts. The
ethanol yields were 0.53 g ethanol per g of mannitol after 11.7 h, and 0.61 g ethanol per g of
mannitol at 21.9 h. Further research by Adams et al. [15] explored ethanol production using
laminarin from Saccharina latissima, (a brown macroalg) fermented with Saccharomyces
cerevisiae (a yeast) with a range of pre-treatments. The results indicated that pre-treatments
prior to fermentation were not required for the fermentation process, and higher ethanol
yields were achieved in untreated fermentation than those with altered pH or temperature pre-
treatments, both for fresh and defrosted macroalgae samples. The highest ethanol yield achieved was 0.45% (by volume) [15]. These findings are contrasted with pretreatment research for other groups of macroalgae. Wi et al. [12] investigated fermentation pretreatments for a red macroalgae species exhibiting high carbohydrate contents (typically 23% galactose and 20% glucose) known as Ceylon moss (*Gelidium amansii*). The results found using sodium chlorite prior to enzymatic saccharification, glucose yields of up to 70% were obtained, while only 5% glucose yields were attained without pretreatment. The research also found that efficiency of enzymatic hydrolysis was significantly improved by sodium chlorite pretreatments. This demonstrates the additional potential of pretreatment methods for increasing the scope of macroalgae species suitable for farming for bioethanol production. A study by Ge et al. [29] explored the use of macroalgae floating residue wastes from the *Laminaria japonica*, (a brown algae) alginate industry for ethanol production and the use of diluted sulphuric acid pretreatments and enzymatic hydrolysis consisting of cellulose and cellobiose. The research found the residues exhibited high cellulose, low hemicelluloses, and low lignin contents, and determined that existing farm residues were a promising feedstock for bioethanol production, and that cellulose in processing wastes including floating residues are successfully hydrolysed to produce glucose [29]. These results suggest that in addition to farming of *Sargassum*, additional species (post treatment) and wastes from existing food-grade production may be suitable input streams to supplement both macroalgae and conventional fermentation feedstocks.

4. *Sargassum* spp. as bioethanol feedstock in Pacific island nations

The genus *Sargassum* is widely distributed in tropical and subtropical seas. It is the most dominant and abundant alginophyte in tropical areas. In the Philippines, the *Sargassum* spp.
are the largest among the marine algae [18], and are abundant over rocky, wave exposed, or sheltered areas of the country [30]. The beds of *Sargassum* usually occur near coral reefs where they attach to rocky substrates along reef margins [18]. More than 20 *Sargassum* spp. have been documented in the Philippines [31], the most common include *S. crassifolium*, *S. cristaefolium*, *S. oligosystum*, *S. binderi*, *S. cinctum*, *S. feldmannii*, *S. hemiphyllum*, *S. polycystum*, *S. paniculatum* and *S. siliquosum* [32]. Montaño [33] reported that there are at least 50 distribution sites for *Sargassum* in the Philippines, however, at present there is no commercial production for alginate from *Sargassum* in the Philippines, although pilot studies have been completed [32].

Whilst commercial macroalgae farming is common in the coastal areas of Jolo, Tawi-tawi, Zamboanga del Norte, Zamboanga del Sur, Palawan, Bohol, the Visayas, and Mindanao, *Sargassum* spp. are not currently in production. According to Trono [32], the current harvesting of local stocks of *Sargassum* is minor and limited to certain areas in Northern Mindanao and Visayas. Currently, the most common use of *Sargassum* spp. in the Philippines is as a wrap to maintain the freshness of fishery catches, while minor amounts are used as a feed for pigs and cattle in coastal areas, or dried for export as animal feed [30,32]. Therefore, as *Sargassum* spp. markets are underdeveloped and minimally utilised at present relative to other local macroalgae, farming of the genus might successfully reduce the pressure on existing food production by generating a bioethanol feedstock supply for island nations.

Outside of the Philippines, *Sargassum* spp. have received attention, especially in Japan. Aizawa [13] described a project proposal of mass macroalgae bioethanol production in Japan canvassing the development of extensive farms of *Sargassum horneri*. The proposal modelled the use of 4.47 million km$^2$ of unused areas of the exclusive economic zone and maritime
belts of Japan. Aizawa [13] stated conversion efficiencies from one tonne of raw *Sargassum horneri* (90% moisture, 5.8% carbohydrate) when dried and fermented to approximately 29.6 kg, or 38 L of bioethanol, based on theoretical conversion for alginate with a productivity rate of 3,348 t *Sargassum* km\(^{-2}\) (~9 g m\(^{-2}\) day\(^{-1}\)) using deepwater floating technology. Using the yield and conversion assumptions of the Aizawa et al. [13] research of 38 L t\(^{-1}\) of raw feedstock, in theory the Philippines will need to farm and harvest around 5,761,000 t of *Sargassum horneri* to have achieved the 219 ML annual fuel demand for 2010. Considering that the Philippines farmed 1,666,000 t of macroalgae in 2008, currently expanding at around 150,000 t yr\(^{-1}\), with large available production areas remaining, it is not an unrealistic option to develop a new non-food bioethanol macroalgal industry on the back of current mariculture capability.

### 5. Conclusions

Macroalgae represent an unrealised potential to expand existing mariculture industries, and to diversify gasoline supply from mineral fuel imports to domestic bioethanol producers in Pacific island nations. However, industrial-scale marine macroalgae culture requires significant basic research and development for species and cultivar selection, in addition to harvesting and pre-processing technology investment [34]. Furthermore, the development of efficient and cost-effective fermentation processes, and post fermentation markets for macroalgal waste biomass requires further research. The investment stimulus in the Philippines from the Biofuels Act, and the impetus to mitigate both mineral fuel and biofuel imports may provide such an incentive. Nevertheless, the authors recommend a targeted and collaborative range of initiatives focussing on each point in the supply chain from farmer to biorefinery to explore the technical and commercial potential of this new industry.
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Table captions

Table 1: Projected bioethanol demand, based on projected gasoline consumption in the Philippines. Source: [6].

Table 2: Comparisons of yield, hydrolysable carbohydrate, and potential bioethanol production between major terrestrial bioethanol crops and macroalgae. Source: [15].

Table 3: Proximate analyses of Philippine Sargassum spp. Sources: [23a,24b].

Table 4: Chemical composition of Ascophyllum nodosum. Source: [21].