Chapter

Comparative Analysis of Bioethanol Production from Different Potential Biomass Sources in the Philippines

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Abstract

To pursue the continuous implementation of the bioethanol blending mandate by the Philippine Biofuels Law, part of the roadmap of the National Biofuels Board (NBB) through the Department of Energy (DOE) is to find a sustainable feedstock. This is due to the deficit in locally produced bioethanol as there is an insufficient supply of currently used feedstock, sugarcane. There are several biomasses available in the country with components viable for ethanol fermentation. Aside from sugarcane, these include sweet sorghum and cassava (first-generation), rice straw and corn stover (second-generation), and macroalgae (third-generation). Among which, sweet sorghum can be considered as the best complementary feedstock to sugarcane as its syrup can be directly fermented to produce bioethanol. Considering its maximum bioethanol potential yield of 100 L/ton for two croppings annually, a comparably low production cost of PhP 36.00/L bioethanol was estimated, competitive enough with the PhP33.43/L bioethanol from sugarcane. Aside from finding a promising feedstock, the bioethanol production volume in the country must be increased to meet the demand through either working on the optimum processing conditions to increase the capacity utilization from the current 77.9% or through installation of additional distilleries.

Keywords: bioethanol, biomass, fermentation, lignocellulosic, saccharine, starchy feedstocks

1. Introduction

The use of biofuels in the Philippines was initiated due to the oil crisis of the 1970s. However, the implementation did not immediately push through as the domestic cost of production of biofuels was higher than the cost of importing oil. Hence, to reduce the biofuels production cost and correspondingly its selling price, the Philippine Department of Agriculture (DA), as a member of the NBB, is tasked to develop a sustainable and viable feedstock for the production of biofuels. For each feedstock assessed based on its availability and accessibility, a suitable and economically competitive conversion technology is applied, usually developed through the research programs of the Philippine Council for Industry, Energy and Emerging Technology Research and Development (PCIEERD) of the Department of Science and Technology (DOST). On the other hand, for the implementing policies supporting the Philippine Biofuels program, the enactment of the Republic Act No. 9367 (RA 9367), also known as the Biofuels Act of 2006, designates specific mandates on government agencies particularly to ensure feedstock supply like sugarcane for bioethanol under the Sugar Regulatory Administration (SRA) and coconut for biodiesel under the Philippine Coconut Authority (PCA) [1].

RA 9367 aims to increase the contribution of biofuels in the country's energy mix, specifically in the transport sector, by reducing its dependence on fossil-based fuels, mitigating climate change while creating more job opportunities for the national socio-economic development. The law took effect last February 6, 2007, and after two years, 2% by volume blending of biodiesel with diesel and 5% by volume blending of bioethanol with gasoline were implemented. The monitoring of this blending mandate and the evaluation of policy execution are by the NBB, headed by the Philippine DOE. The law also encourages investments in the biofuels sector by providing incentives in the production, distribution and use of locally produced biofuels. Incentives include zero specific tax per liter of volume for biofuels component, exemption from value added tax (VAT) on the sale of raw material used in the production of biofuels, exemption from wastewater charges of all water effluents from the biofuels production in accordance with the Republic Act No. 9275 (Philippine Clean Water Act of 2004), and high priority from government financial institutions if engaged in production, storage handling and transport of biofuels feedstock, biofuels and blending with petroleum as certified by the Philippine DOE [2]. Additional incentives such as income tax holiday (ITH), duty-free importation, and low-income tax rate of 10% after the ITH may also be availed as implied by the Republic Act No. 9513 or the Renewable Energy Act of 2008. In tandem with these and with the aim to further boost the country's rural economy, the Joint Administrative Order No. 2008–1 was released providing guidelines governing biofuels feedstock production and emphasizing that feedstocks for biofuels production must only be sourced locally [3].

Currently, DOE has maintained the ethanol and biodiesel blends at 10% and 2% by volume, respectively and still unclear whether the blending targets based on the RA 9367 will be increased for the succeeding years. Until now, the insufficient feedstock supply is one of the major dilemmas in the ethanol industry. From the utilization of sugarcane, the ethanol industry players have been in transition to using molasses as source of bioethanol fuel. Molasses, as a byproduct of sugar manufacturing process from sugarcane, also has a limited supply resulting to unwarranted escalation in the price of gasoline when blended with bioethanol. Same case with the biodiesel industry, there is a fluctuation in the price of *copra*. *Copra* refers to the dried coconut kernel or meat from which the oil that is processed to biodiesel is obtained. Unlike sugarcane or molasses, there is oversupply of *copra*. Hence, the gradual upward adjustments in the biodiesel blend would not be a problem.

To provide sufficient feedstock to existing ethanol plants, the joint Oversight Committee on Energy of the Philippine Congress and Senate arrived with the interim solutions last year 2019. These include exploring the high yielding varieties of sugarcane and revisiting the available feedstocks in the country for bioethanol production. There is also a continuous conduct of research and development on feedstock sources as imposed by DOE through its Philippine Energy Plan on biofuels for the year 2020 to 2040 [4]. Some of the biomass under research and deployment for bioethanol production include sugarcane, cassava and sweet sorghum for first-generation, agricultural and forest residues such as rice straw and corn stover for second-generation, and macroalgae, commonly known as seaweeds for third-generation biofuel. Hence, this book chapter is a consolidation of information on the potential of different biomass available in the Philippines that can be utilized as feedstock for bioethanol production. A brief overview of the bioethanol market in the Philippines is also discussed which supports the need for complementary feedstocks to sugarcane for the different generations of bioethanol. The criteria for selection of a good feedstock for bioethanol, challenges that maybe encountered upon using the biomass as starting raw material, and appropriate conversion technologies are also provided.

2. Bioethanol situation in the Philippines

2.1 Bioethanol market size and trends

A joint sales report by the Chamber of Automotive Manufacturers of the Philippines, Inc. (CAMPI) and Truck Manufacturers Association (TMA) showed a boost in vehicle sales of 3.5% relative to last year 2018 [5]. The increase in purchase of cars, motorcycles, tricycles, and utility vehicles had been attributed to the increasing income of the middle class and improvements in the infrastructure. In addition, the lowering of the amortization costs of most vehicles and lower interest rate make the acquisition of these vehicles more affordable to many. This trend is projected to continue in the future. This surge in the vehicle industry sales brings in the transport sector as the most energy intensive sector contributing the 37.2% in the country's final energy demand. This corresponds to 39.9% gasoline's share out of the 96.4% bulk share of petroleum products used as the sector's primary fuel. The continuous growth in gasoline consumption brought by rapid urbanization and motorization would require larger volume of ethanol [6].

For the year 2020, a higher blend of 20% should have been imposed according to the Philippine Energy Plan 2016–2030 (**Figure 1**), with the goal also to increase the bioethanol blending up to 85% in 2030 [2, 6]. The planned increase is still under review due to several factors such as high feedstock and production cost, insufficient and competing feedstock supply, inadequate bioethanol production plant capacity, as well as importation and price regulations. To meet the country's ethanol demand, the Biofuels Act allowed the importation of bioethanol within four (4) years from the effectivity of the law and only to the extent of the shortage as may be determined by the NBB [7]. Imports were sourced from the United States of America, Australia, and South Korea [8]. This defeats the purpose of the National Biofuels Program which seeks to reduce dependence on imported oil. Even beyond the imposed period and in the current year, the bioethanol from local sources is still insufficient to meet the demand resulting to huge importation (**Figure 2**) despite the disallowance of the law.

There are twelve (12) accredited bioethanol producers with a total production capacity of 380.50 million liters since 2018 (**Figure 3**) [9, 10] and as of the end of March 2020 (**Table 1**) [11]. These refineries operate at 77.9% capacity (**Figure 3**) [9, 10]. Additional three (3) plants with a total capacity of 113 million liters will be on-stream supposedly in 2020, two are still under construction and one completed

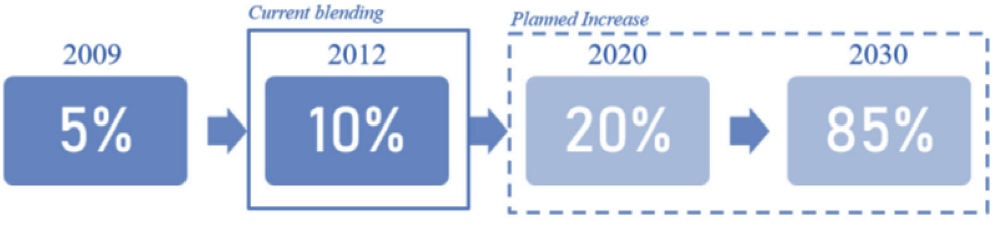

Figure 1.
Mandated bioethanol blending rate based on the Biofuels Act of 2006.

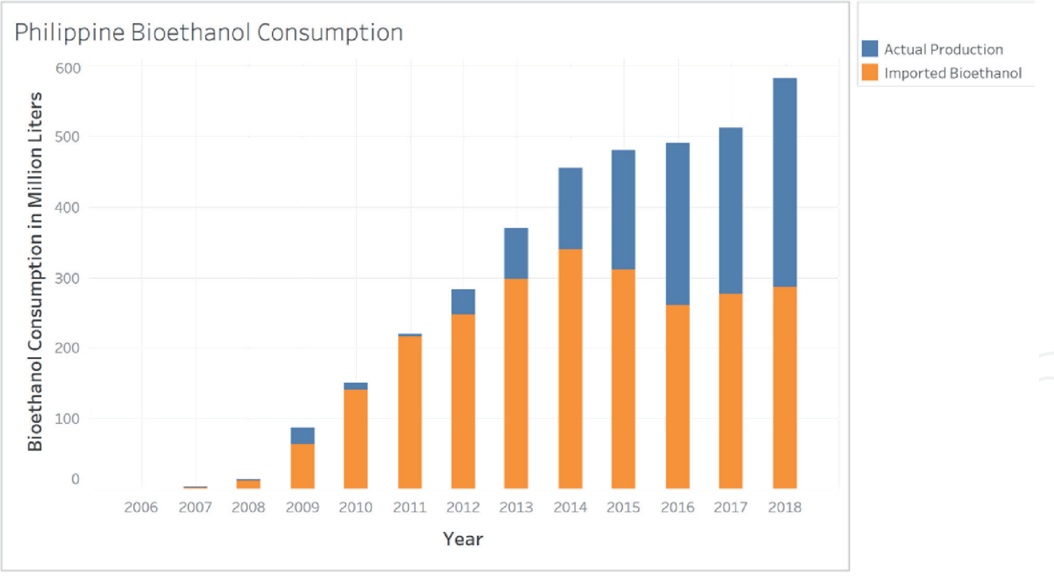

Figure 2.
Bioethanol consumption in the Philippines, 2006–2018.

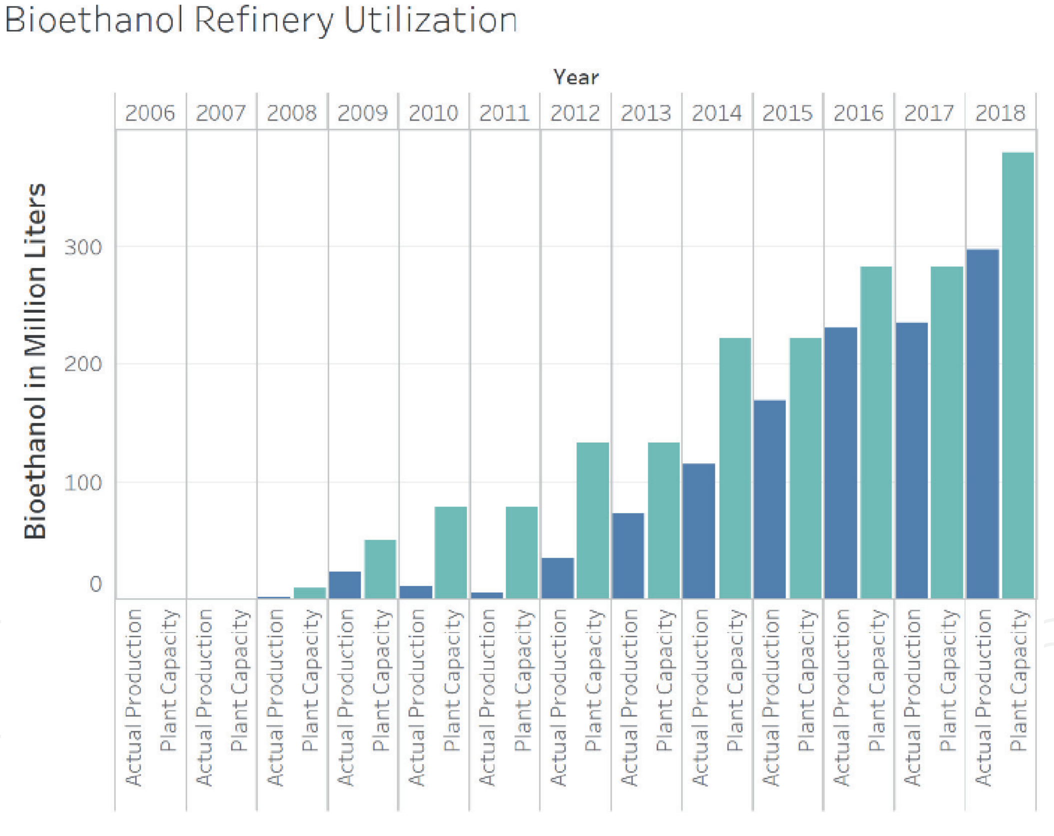

Figure 3.
Bioethanol refinery capacity utilization in the Philippines, 2006–2018.

the pilot plant test [11]. This leads to a total of 493.5 million liters production capacity, still lacking to meet the projected bioethanol demand of 847.61 million liters (supposedly at 20% blending rate) for the current year.

From 2007 to 2014, majority of bioethanol produced in the Philippines was sourced from sugarcane (**Figure 4**). Due to the SRA's mandate on prioritizing sugarcane for sugar production and the increasing demand in domestic bioethanol, the share of molasses (a by-product in sugar production) in the bioethanol feedstock mix increased in the recent years. In 2018, about 99.2% of domestic bioethanol was produced from molasses [9, 10].

Bioethanol producers	Refineries' location	Plant capacity (MLPY)
1. Absolut Distillers, Inc.	Lian, Batangas	30
2. Balayan Distillery, Inc.	Calaca, Batangas	30
3. Far East Alcohol Corp.	Apalit, Pampanga	15
4. Green Future Innovations, Inc.	San Mariano, Isabela	54
5. Progreen Agricorp, Inc. - Nasugbu	Nasugbu, Batangas	30
6. Progreen Agricorp, Inc. – Balayan	Balayan, Batangas	66
7. Kool Company, Inc.	Talisay City, Negros Occidental	30
8. Leyte Agri Corp.	Ormoc City, Leyte	9
9. Roxol Bioenergy Corporation	La Carlota City, Negros Occidental	30
10. San Carlos Bioenergy, Inc.	San Carlos City, Negros Occidental	40
11. Universal Robina Corporation	Bais City, Negros Oriental	30
12. Victorias Milling Company, Inc.	Manapla, Negros Occidental	16.5

Table 1.
List of accredited operational bioethanol producers in the Philippines as of 31 march 2020.

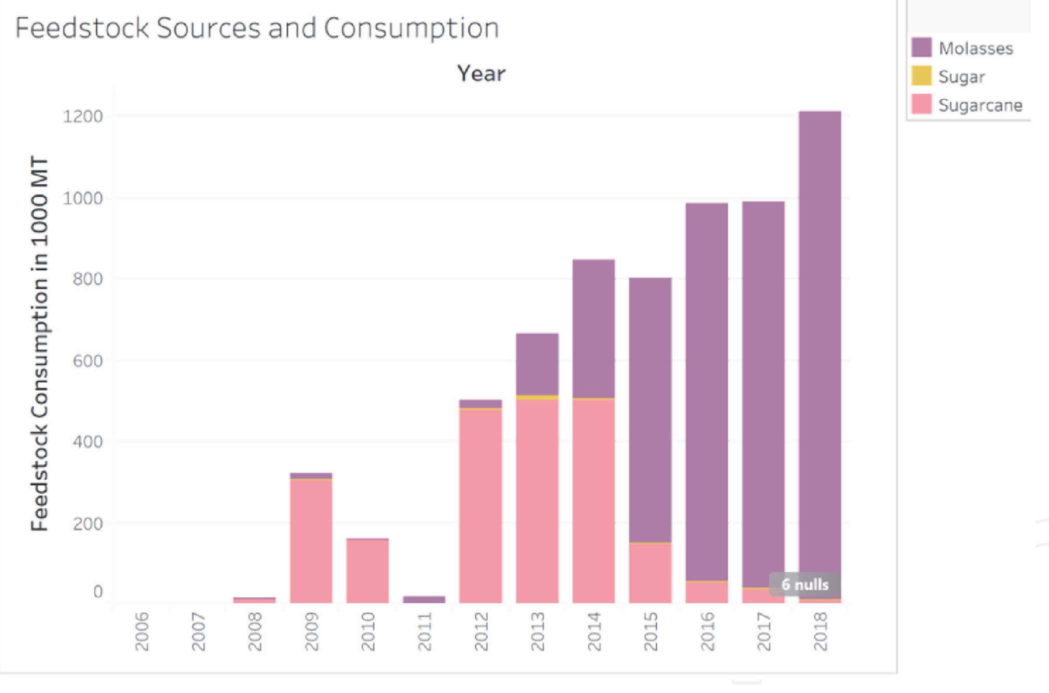

Figure 4.
Consumption of bioethanol feedstocks in the Philippines, 2006–2018.

The bioethanol price index in the Philippines is determined by the SRA bi-monthly and is based on the equivalent prices of sugarcane and molasses, the two major bioethanol feedstock sources in the country. **Figure 5** shows the monthly average prices of sugarcane, molasses, and bioethanol from 2011 to 2020 [12]. The bioethanol price shows a general slight increase during this period, which can be attributed to the increase in molasses price. The price of molasses has become more expensive than sugarcane during the period in which its share on the bioethanol feedstock mix has increased. Before, molasses was an under-utilized by-product of sugar mills in the country, but it has found value as a bioethanol feedstock after the implementation of the RA 9367. In the point of view of the sugar mills, the increase in molasses price is

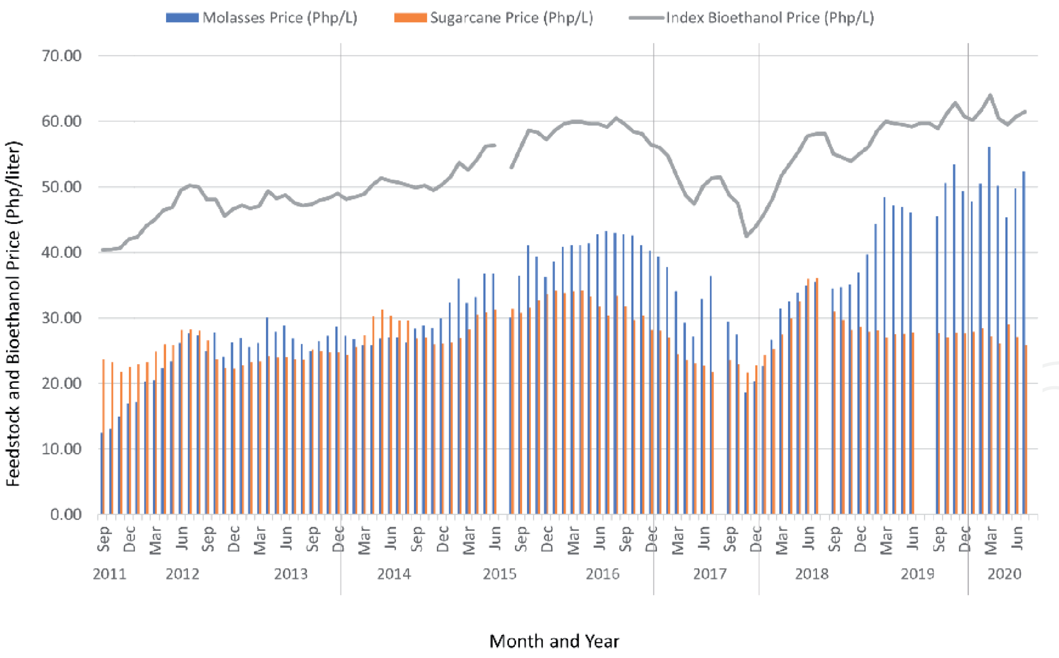

Figure 5.
Bioethanol price trend against feedstock prices, i.e. molasses and sugarcane. Gaps in the chart represent end of milling season.

advantageous due to the added income that it brings to the mills. But for the bioethanol industry, an increase in molasses price and in general, an increase in feedstock price, would mean an increase in the bioethanol selling price. Currently, bioethanol is more expensive than gasoline. Perhaps, this is one of the bottlenecks in increasing the bioethanol blend as it will drive the price of blended gasoline to increase. One of the possible ways to dampen the increase in feedstock price is to diversify feedstock sources and to increase the domestic bioethanol production capacity.

2.2 Bioethanol industry outlook

In the next 20 years, the country is still expected to heavily rely on petroleum products for fuel (**Figure 6**). With the projected increase in bioethanol blend, its demand is also expected to increase to 2616.38 million liters in 2040 [8]. More

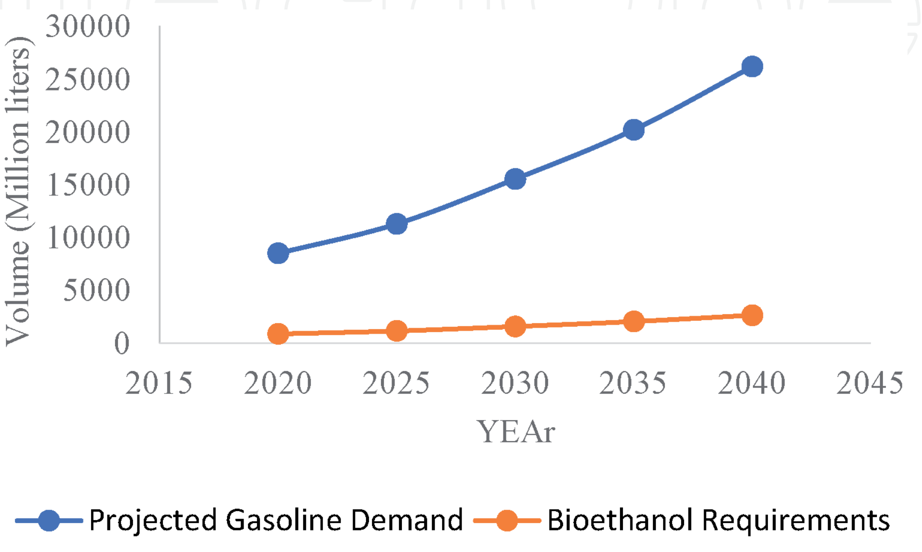

Figure 6.
Bioethanol demand outlook for 2020–2040.

Year	Gasoline requirement (MLPY)	Bioethanol requirement (MLPY)	Additional plants needed
2020	4302	860	15
2021	4381	876	1
2022	4467	893	
2023	4559	912	1
2024	4657	931	
2025	4663	933	1
2026	4757	951	
2027	4843	968	1
2028	4937	987	
2029	5005	1001	1
2030	5052	1010	

Table 2.
Additional refineries needed based on projected gasoline consumption and bioethanol requirement at 20% blending rate for the year 2020–2030.

distilleries will be needed to meet this demand as well as land area to be planted for additional bioethanol feedstock.

In the projections by the Philippine DOE, the total gasoline consumption would grow annually by 1.9%, while bioethanol at 9.7%. To meet the 2020 bioethanol demand at 20% blend without importation, the Philippines necessitates 15 additional distilleries. However, starting from 2021 and every other year, there is a need to put up five (5) more bioethanol plants to meet the blending requirements in 2030 (**Table 2**) [9].

3. Suitability assessment and challenges of producing bioethanol from biomass sources

3.1 Abundance and availability of feedstock supply

There are three generations of feedstocks that can be used as source of bioethanol and these feedstocks can be further classified based on the substrates present on their structure, suitable for ethanol conversion. One of these includes saccharine-based feedstocks or those containing sugars readily fermentable into bioethanol. Examples of these saccharine feedstocks are sugarcane and sweet sorghum. There are also land-based feedstocks that must undergo pre-processing conditions to make the substrates cellulose and hemicellulose available for ethanol fermentation. These include agricultural and forest residues. On the other hand, the third-generation biofuel feedstock such as macroalgae, commonly known as seaweed, can thrive and expand without taking the land used for agriculture. With the aim also to find a sustainable source of fuel that will not compete with food production, macroalgae's potential as feedstock was explored.

As shown in **Table 3**, sweet sorghum has the highest ethanol productivity among the potential feedstocks, based on the availability of lands for cultivation and with the assumption of maximum full biomass conversion to bioethanol. Sweet sorghum is drought tolerant and can survive in a range of environmental conditions making it a suitable complementary feedstock to sugarcane. Like sugarcane, sweet sorghum can be regenerated through ratooning. It has a shorter life cycle of four (4) months and its ratoon can be harvested for as early as three (3) months, relatively shorter compared with the 10-month crop duration of sugarcane [13]. This crop could be the solution on the issues of land availability for planting sugarcanes in the Philippines.

Rice straw is the 2nd biomass with the highest potential as source of bioethanol based on **Table 3**. If the establishment of bioethanol plants using rice straw will be realized, this biomass can contribute to about 11% of the total bioethanol demand of the country by 2030 at 85% blending rate. However, currently, there are a lot of emerging applications of rice straw which may lead to competing use of the biomass for ethanol fermentation. Rice straw can be also utilized for practices like soil improvement through carbonization and composting, fuel for power generation, mushroom production, animal feeds and as starting material to produce silica and bio-fiber [17].

In terms of maximum bioethanol potential, the seaweed *Sargassum* has the highest recorded yield with 467 L bioethanol per ton biomass. *Sargassum* is a brown macroalgae which belongs to the phylum *Phaeophyta.* It has a high content of degradable carbohydrates to bioethanol such as alginate, laminaran, mannitol, fucoidan and cellulose [18]. Most of these seaweeds are found in cold waters and

Feedstock	Biomass production yield (ton/ha)	Maximum bioethanol potential yield (L/ton)	Ethanol productivity per area (L/ha)	Potential available area (ha)	Total ethanol per available area (L)	Sources
First generation						
Sugarcane	60	65	3900	4990 (existing SRA certified areas)	19.11 M	[12]
Sweet sorghum	50	100	5000	1.21 M (idle lands suitable for sweet sorghum	6.05 B	[14]
Cassava	8	178	1424	217,978	310 M	[14]
Second generation						
Rice straw	2.6 (dry season); 3.5 (wet season)	158	964	488,500	471 M	[15]
Corn stover	5.6 (dry season; 7 (wet season)	176	2218	94,900	210 M	[15]
Third generation						
Macroalgae *(Sargassum* spp.)	33.48	467	15,635	Marine area and bioethanol productivity depend on the farm size for cultivation of seaweed		[16]

Table 3.
Bioethanol production potential of feedstock options in the Philippines.

grow in the intertidal belt and in the upper littoral region [19]. However, seaweed farming is encouraged for feedstock acquisition to avoid compromising and threatening the balance in the marine ecosystem because of uncontrolled harvesting which happened in 2014. It was only in 2018 when the Bureau of Fisheries and Aquatic Resources (BFAR) lifted the ban and allow fisherfolk to collect, sell, trade and transport *Sargassum* through Administrative Order 250–2, subject to seasonal restrictions and permit requirements [20].

3.2 Low product inhibition and reduced byproduct formation

In the Philippines, fermentation is the commonly used process in producing ethanol from various types of biomass. It is a biochemical conversion of biomass into sugars using acids or enzymes and the transformation of these sugars into ethanol and other chemicals with the aid of yeast, typically *Saccharomyces.* Parameters that have relative effects on fermentation include pH, temperature, sugar concentration, types of yeast, variation in medium constituents and in the incubation time for inoculum preparation [21]. Employing optimum fermentation conditions increases the yeast growth rate and metabolism of substrates, achieving high ethanol yield and reducing byproduct formation.

Saccharomyces is highly specific in converting glucose units to ethanol. However, no biomass contains purely glucose. Thus, low substrate concentration corresponds to low product formation. Since the total sugar in the biomass is regarded as the sum of glucose, fructose and sucrose [22] and also comprise of other types such as xylose, ribose, arabinose, sorbose, galactose, mannose, etc., high amounts of substrates remain unconverted. For some feedstocks such as starchy crops, dextrification using an enzyme α-amylase is necessary to hydrolyze first the starch into maltose (Eq. 1). This step is followed by the use of exoenzyme glucoamylase to achieve conversion of maltose into glucose (Eq. 2) for then to be converted to ethanol using *Saccharomyces*. In addition to sugars, there are also salt and sulfated polysaccharides in the biomass structure which inhibit ethanol formation. These are usually removed through chemical treatment prior to fermentation. Nutrient supplementation during fermentation is also done to enhance the activity of the yeast or to improve its substrate consumption rate.

$$2(C_6H_{10}O_5)_n[starch] + nH_2O \rightarrow nC_{12}H_{22}O_{11}[maltose] \quad (1)$$

$$C_{12}H_{22}O_{11}[maltose] + H_2O \rightarrow 2C_6H_{12}O_6[glucose] \quad (2)$$

3.3 Low ethanol production cost

Eq. (3) is the established formula for bioethanol reference price provided for producers who use molasses and sugarcane as feedstocks. The equation is a function of average feedstock price and the processing cost per liter of ethanol produced [3]. Considering these two variables in comparing the different biomass for ethanol production, sugarcane and sweet sorghum are the cheapest with PhP 33.43/L and PhP 36.00/L respectively, because both can be subjected to direct fermentation. On the other hand, the estimated production cost for seaweed-based bioethanol is around PhP 45.45/L as more pretreatment processes are required to degrade the polymers alginate, cellulose, mannitol, and laminarin into reducing sugars prior to fermentation. Highest production costs for cassava, rice straw and corn stover of PhP 64.45/L, PhP 59.39/L and 46.08 PhP/L, respectively (**Figure 7**) are due to use

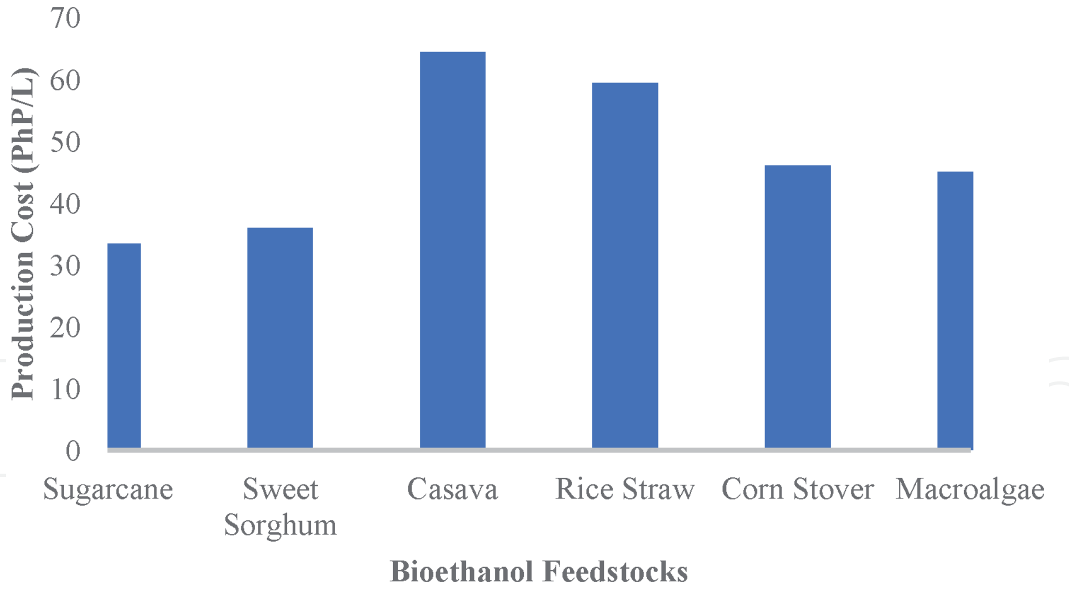

Figure 7.
Ethanol production cost per liter using various biomass.

of enzymes or additional chemicals to saccharify the starch to glucose units before fermentation.

$$EthanolPrice = AverageFeedstockPrice + ConversionCost \tag{3}$$

The low production costs of bioethanol from sweet sorghum and macroalgae lead to a competitive and comparable farmer's potential annual income from cultivating and harvesting these feedstocks, with PhP 50,000/ha per cropping for sweet sorghum and PhP 97,000/ha for *Sargassum* [14, 16].

4. Review on conversion technologies for first to third-generation bioethanol

Bioethanol may be produced from sugary or saccharine feedstocks such as sugarcane and sweet sorghum, starchy feedstocks such as rice and corn, and lignocellulosic feedstocks such as agricultural and forest residues. Bioethanol may also be produced from macroalgae such as *Sargassum*.

The general process flow in producing bioethanol from these feedstocks is shown in **Figure 8**. The juice from sugarcane and sweet sorghum stalks can be directly converted to ethanol via fermentation. Starchy and lignocellulosic feedstocks need to be pretreated and saccharified prior to fermentation adding to the cost of producing ethanol. The pretreatment step is discussed further in Sections 4.1 to 4.3.

The fuel ethanol plant composed of the fermentation, distillery, and anhydrous plant, is the most critical and most complicated part of the processing plant. **Figure 9** shows a schematic diagram of the fermentation plant. It is typically composed of a series of seed culture vessels of increasing volume, pre-fermenter, and fermenters. Nutrients needed by the yeast are added to the reactors and typically composed of urea (150 ppm), di-ammonium phosphate (75 ppm). Magnesium sulfate (35 ppm) and biocide (10 ppm). Sulfuric acid is also added at 0.2 ml per 200 ml mash to maintain the pH at 4.1–4.5. The process starts with the sterilization of the substrate at 70°C for 30 minutes and then cooled. The yeast and the nutrients

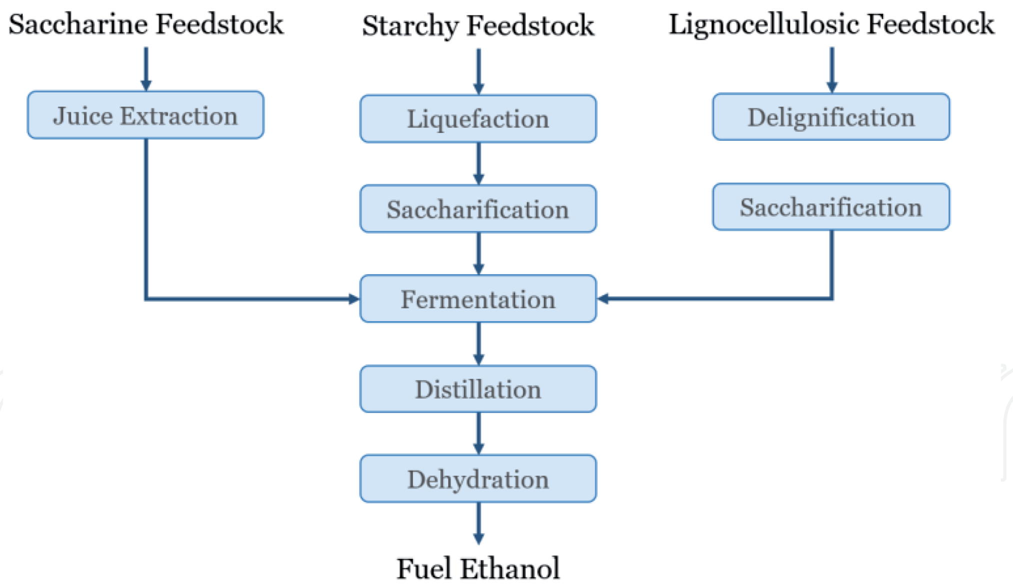

Figure 8.
General process flow of bioethanol production from different feedstocks.

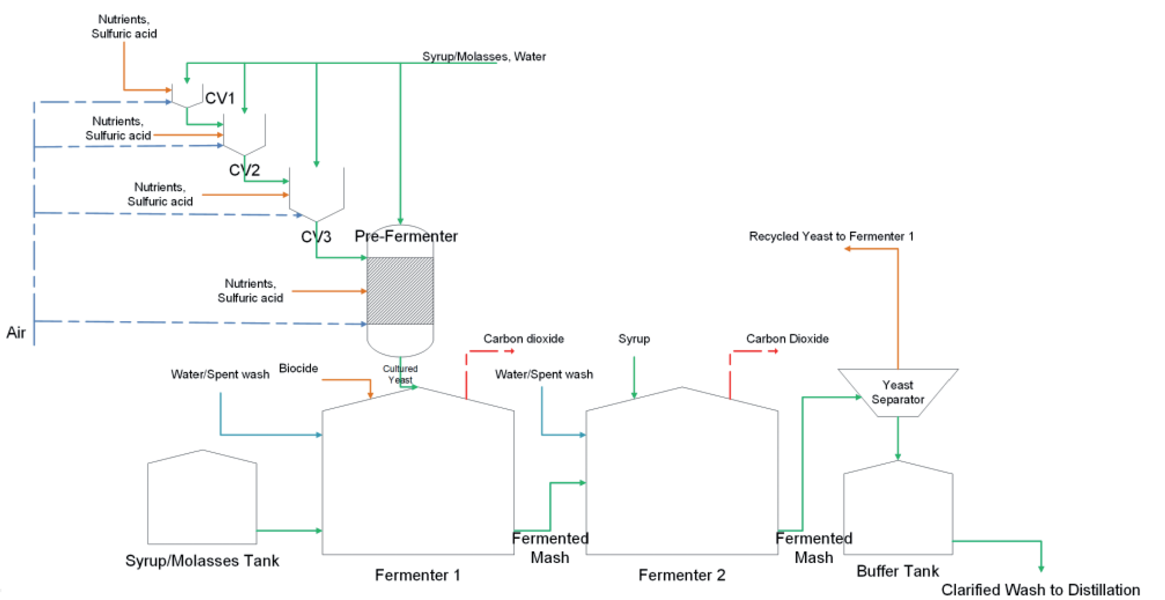

Figure 9.
Schematic diagram of fermentation in bioethanol distillery.

are then added, and fermentation is allowed for 24 hours at 32–34°C. The overall efficiency of the fermentation process is about 80–90% and the alcohol content of the clarified fermented mash is around 7–8% by volume.

The distillation plant, shown in **Figure 10**, is composed of a primary column, de-aldehyde column, and rectifier column. The primary column concentrates the alcohol content of the clarified fermented mash to about 20–30% alcohol by volume. The de-aldehyde then removes the aldehyde side-product from fermentation. The bottoms from this column is composed of 30–40% alcohol, which is fed to the rectifier column to concentrate it to 95–96% alcohol.

The dehydration plant is composed of a recovery column and two-column pressure swing adsorption (PSA) system containing molecular sieves (**Figure 11**). The recovery column removes some water from the rectified spirit, which is then superheated to 140–144°C before feeding to the PSA system. The anhydrous plant produces 99.5–00.95% ethanol with an efficiency of 99.8%.

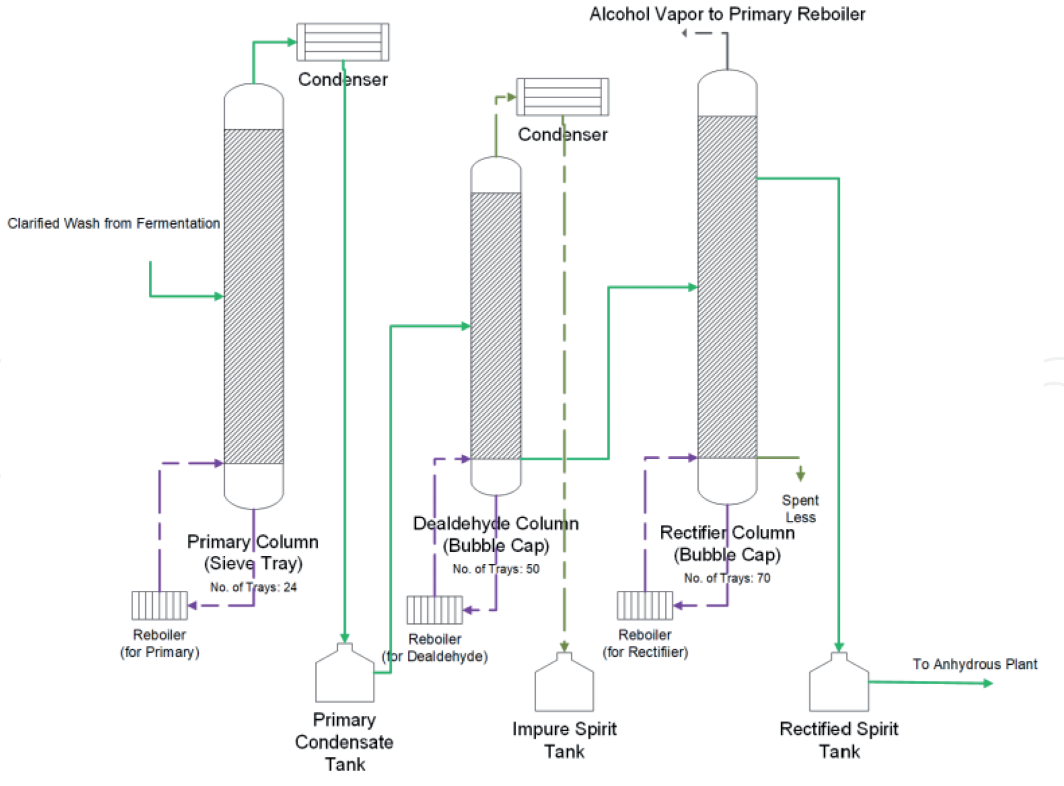

Figure 10.
Schematic diagram of distillation process in a bioethanol distillery.

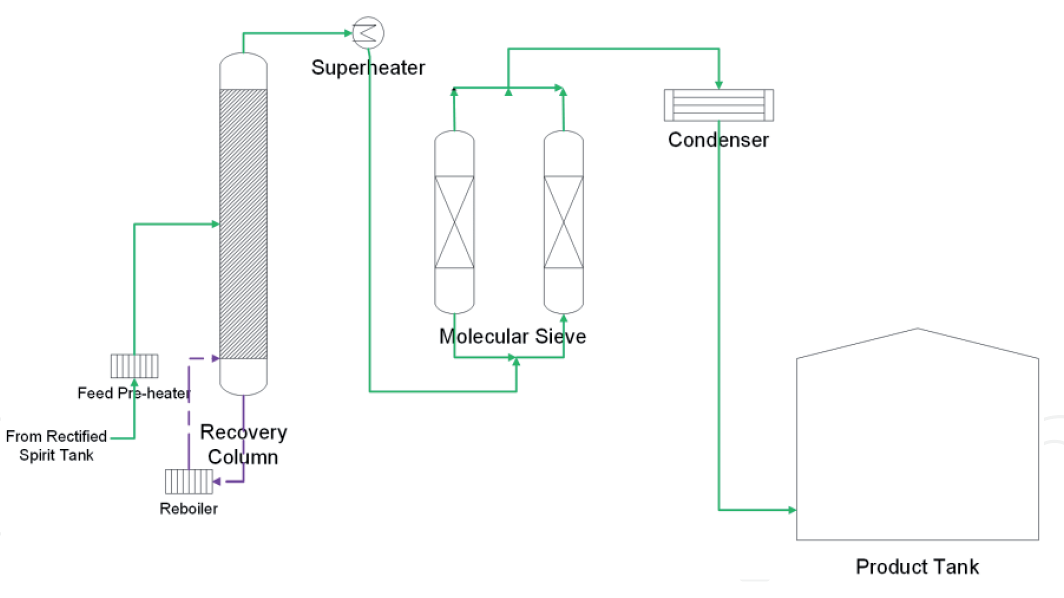

Figure 11.
Schematic diagram of dehydration by pressure-swing adsorption.

4.1 First-generation bioethanol production process

4.1.1 Sugarcane and sweet sorghum (saccharine feedstock)

Sugarcane is a grass grown in tropical and subtropical regions propagated for its sugar. In the Philippines, the sugarcane stalk yield of 60 metric ton per hectare can yield about 65 liters ethanol per metric ton per year. A 7692-hectare sugarcane plantation is needed to supply the feedstock requirement of a distillery with a 30-million-liter ethanol capacity.

On the other hand, sweet sorghum [*Sorghum bicolor* (L.) Moench] is a drought-resistant crop with high agronomic yield and sugar content of stalks. It is considered an alternative to sugarcane as a bioethanol feedstock. It can be harvested after 115 to 120 days, which makes it amenable for multiple cropping through ratooning. Stalk yield can reach 50 metric ton per hectare with an ethanol potential of 100 liters per metric ton per year. A 6000-hectare land planted to sweet sorghum will be needed to support an ethanol distillery producing 30 million liters of ethanol per year [23].

Juice extraction and syrup production from sweet sorghum requires the same operations and equipment in sugarcane processing, which includes cane handling and preparation, milling, juice heating, clarification, and evaporation.

4.1.2 Cassava (starchy feedstock)

Cassava is considered the cheapest among the major starch-based feedstock for ethanol production due to its high starch content (about 74% by weight) and starch-to-sugar conversion ratio. It can be harvested year-round in areas with evenly distributed rainfall. The crop is relatively typhoon and drought-resistant and requires minimum crop maintenance. Cassava tubers can also be chipped, dried, and stored for utilization during periods of lean supply [24].

During the period of April to June 2020, production of cassava from 110,780.04 hectares planted area was recorded at 722.82 thousand metric tons [25]. This is equivalent to a national average yield of 6.52 MT/ha. In ideal production areas for cassava, the yield can reach up to more than 20 metric tons per hectare. Ideal plantation sites are characterized by plain to rolling areas with even rainfall distribution throughout the year and soil types ranging from loam, sandy loam, fine sandy loam and silty clay loam [24].

Based on a distillery plant's capacity of 30 million liters per year, at a conservative estimate of 180 L ethanol per metric ton cassava, an estimated 8333 hectares of cassava plantation would be required to supply the feedstock for the plant's optimal operation [24].

Before processing to ethanol, the freshly harvested cassava tubers should be transformed first into cassava flour through washing, cleaning, peeling, chipping, drying, storage, and milling. The flour is then mixed with water to make a slurry, which is then gelatinized with steam, liquefied with alpha-amylase, and saccharified with glucoamylase.

Liquefaction consists of gelatinization and dextrinization. Gelatinization is the dissolution of starch into a mash by steam cooking. Gelatinization can be done in a steam jet cooker at 120°C at a residence time of only a few seconds. This step requires steam at 138°C and 2 bar pressure. The gelatinized starch then passes through a holding coil at 120°C for 1 minute and a flash tank before undergoing dextrinization. Dextrinization is the breakdown of the gelatinized starch into smaller fragments by means of alpha- or beta-amylase or dilute acid. This step results to the reduction of the solution's viscosity and the production of malto-dextrins. Dextrinization must be done immediately without allowing the solution to cool to prevent recrystallization of starch. The last pretreatment step prior to fermentation is saccharification, which can be accomplished by addition of glucoamylase and thin slops to the liquefied mash. This process is undertaken at 60°C and pH 4.5 for 30–60 minutes. The saccharification reaction is particularly fast up to 70% dextrose; as the 95% dextrose is reached, it starts slowing down [24].

4.2 Second-generation bioethanol production process

Second-generation feedstocks for bioethanol production include non-food sources such as agricultural and forest residues and grasses. They are also called lignocellulosic feedstocks since these materials are composed of lignin, cellulose, and hemicellulose. Lignin cross-links with other cell wall component making the hydrolysis of cellulose and hemicellulose to their component monomeric sugars difficult. Delignification and pretreatment are therefore required to make the cellulose and hemicellulose fraction amenable to hydrolysis and fermentation.

Pretreatment can be done physically, chemically, and biologically. Physical pretreatment involves the disruption of the lignocellulose structure by physical and mechanical means to increase the surface area of the biomass and provide access to cellulases upon hydrolysis. Physical pretreatment methods include uncatalyzed steam explosion, liquid hot water, mechanical comminution, and high energy radiation. Chemical pretreatment involves the use of chemicals to delignify the biomass and sometimes to dissolve the hemicellulose fraction to enhance enzymatic digestibility of the cellulose. This pretreatment method includes hydrolysis via concentrated acid and dilute acid, alkaline pretreatment, ammonia fiber/freeze explosion (AFEX), organosolv, pH-controlled liquid hot water, and ion liquids (ILs) pretreatment. Biological pretreatment used wood-degrading microorganisms to modify the chemical composition and/or structure of lignocellulosic biomass and make it more suitable to enzyme digestion [14].

Rice straw and corn stover are examples of lignocellulosic materials. They are agricultural wastes; thus, their cost is low if they are to be used as feedstock for bioethanol. However, the high cost of pretreatment makes them unattractive for bioethanol production. For every ton of rice produced, a ton of rice straw is also produced. At 20% moisture content, rice straw's ethanol potential is about 158 L per metric ton. At a yield of 2.6 metric ton of rice per hectare during the dry season, about 50,215 hectares of land planted to rice is needed to support an ethanol plant with a capacity of 30 million liters per year. For corn stover, 20,877 hectares of land planted to corn is needed to provide enough feedstock to an ethanol plant producing 30 million liters per year considering that 3.92 metric ton corn stover can be obtained per hectare and 176 liters ethanol can be produced per metric ton of corn stover [26].

4.3 Third-generation bioethanol production process

Over 80 species of *Sargassum* are found in the Philippines, widely distributed in the islands of Luzon, Visayas and Mindanao. It has several local names like *Aragan, Boto-boto, Lusay-lusay* and *Samo.* In the old days, *Sargassum* is used as a wrapper to maintain the freshness of fish and other sea commodities. It also functions as animal feed, a healthy beverage, fertilizer and other agricultural uses. Nowadays, the use of these species has been lessened because of modern technologies and concerns on preservation of marine biodiversity [27].

The most notable characteristic of brown macroalgae, *Sargassum* in particular, is the absence of lignin in its cell walls [18]. Lignin, a component of biomass which holds typically the celluloses, is a protective material that provides rigidity to the biomass and the resistance from microbial attack [28]. In **Figure 12**, even though there is no need for delignification process, series of pretreatment methods are necessary to convert the target polymeric constituent to bioethanol.

The seaweed shall undergo physical treatment such as drying and milling for the biomass to be more susceptible to enzyme or chemical. Mannitol can be precipitated through hot (i.e. boiling) water extraction at 96.1% efficiency. Alginic acid, on the other hand, is produced by mixing the seaweed with 4% w/w sodium bicarbonate solution. The supernatant that will be collected after treatment should be stored at 4°C prior to precipitation of alginic acid by adding sulfuric acid. Laminarin can be extracted through sequential hydrochloric acid and ethanol treatment at a working temperature of 70°C. Hydrolysis of cellulose and laminarin can be carried out using

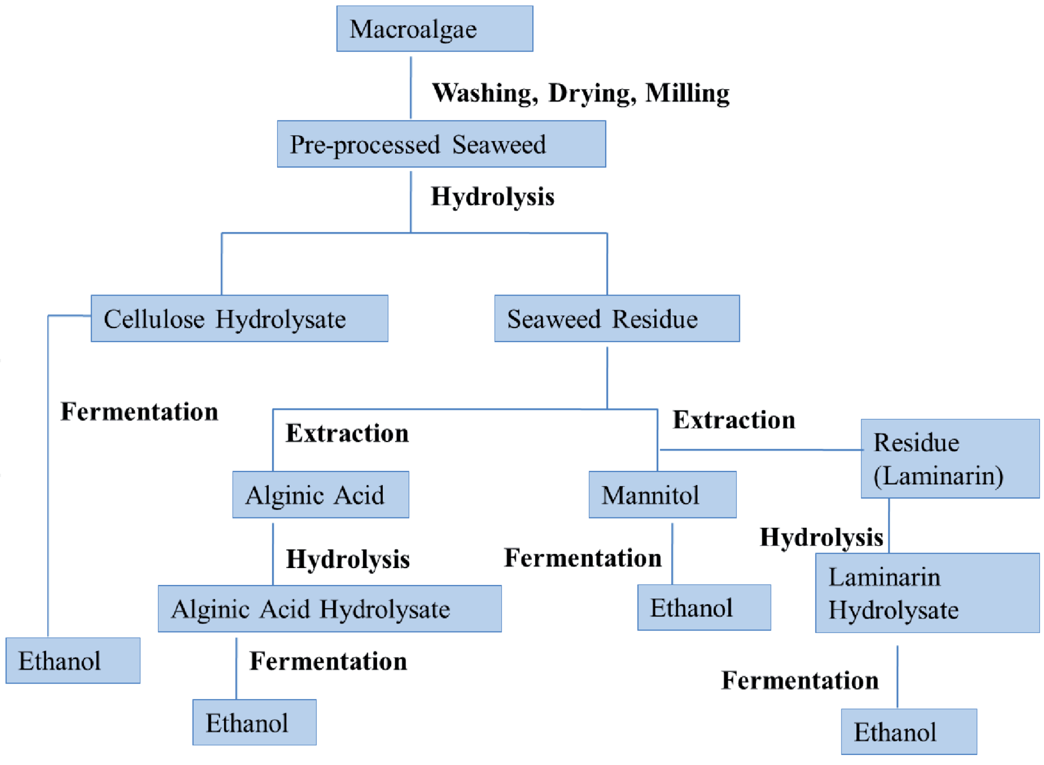

Figure 12.
Process flow of bioethanol production from Sargassum.

the enzyme *cellulase* at 50°C, while the alginic acid using the enzyme lyase at 37°C. Mannitol as a sugar alcohol can be directly fermented into bioethanol [29].

Upon fermentation and purification, a maximum ethanol yield of 467 L per ton dried seaweed could be attained from *Sargassum* with the following composition (w/w): 21% laminarin, 5% mannitol, 32.65% alginic acid and 6.20% cellulose [16]. To produce 30 million liters of bioethanol, which is the typical capacity of distilleries established in the Philippines, a cultivation area of 1918 ha of *Sargassum* is needed [29]. The seaweed composition dictates the resulting ethanol yield. The variation in composition depends on the maturity of the seaweeds. The maturity can be assessed based on the length of the plant from the holdfast to the tip of the longest shoot. The average of increase in lengths was referred as the periodic mean thallus length. The maturity is also influenced by the habitat as the rocky coralline environment of the sea was reported to be favorable for *Sargassum* growth [30].

5. Recommendations on enhancing biomass use for bioethanol production

There are two major gaps in the Philippine bioethanol industry: insufficient feedstock availability and the high domestic ethanol price due to the inefficiency of the process. In selection of complementary feedstock to sugarcane, the potential of crops and their residues should be screened out based on three sustainability criteria: social, economic, and environmental aspects to ensure that the implementation is attainable in the long run. In coordination with an agriculturist, best farm practices and agronomic conditions when the crops should be harvested considering its substrate content (i.e. through sugar analysis) should be recommended. On the processing side, it must be ensured to reduce the byproduct generation by optimizing the fermentation efficiency or the microbial activity and/or improving the pretreatment for lignocellulosic and starchy feedstocks. For agricultural crops as starting raw materials, yield intensification or breeding of good crop varieties are recommended for sufficient feedstock supply. Identification of potential cultivation areas for expansion should also be initiated to continuously sustain the bioethanol blending mandate. Policy support is also one of the most significant on these renewable energy efforts, through concerned agencies headed by the National Biofuels Board.

6. Conclusions

The enactment of Philippines RA 9367, also known as the Biofuels Act of 2006 makes the country the pioneer in biofuels blending in the Southeast Asia. The law mandates the blending of bioethanol to all gasoline sold in the country which is currently at 10%. However, the bioethanol demand was not met due to insufficient supply of locally sourced bioethanol. Hence, the country resorted to importation to sustain the implementation of RA 9367. DOE which serves as the lead agency of NBB developed roadmap and issued policies to address the feedstock concerns on bioethanol production. These include the proposal for an improved breeding program for sugarcane which is currently used as feedstock for bioethanol. Another goal is to find complementary or alternative feedstocks through extensive research and developments.

In this chapter, the criteria for selecting an ideal feedstock for bioethanol production was based on the abundance and availability of feedstock supply, low product inhibition and reduced byproduct formation, and low ethanol production cost. Upon considering the maximum bioethanol potential and available area for harvesting, the following biomass is recommended for producing bioethanol: sweet sorghum (first-generation), rice straw (second-generation), and macroalgae (third-generation). Among these three, sweet sorghum has the lowest ethanol production cost comparable to sugarcane. Hence, it can be regarded as good complementary feedstock to sugarcane for ethanol production.

The potential of other biomass as source of bioethanol can still be enhanced by applying the appropriate conversion technologies and by working on the optimum conditions of the five (5) major processes: Pretreatment, Saccharification, Fermentation, Distillation and Dehydration. The pre-processing methods of the biomass vary depending on its compositional structure (i.e. saccharine, starchy or lignocellulosic). Aside from the aim of increasing the process efficiency, technical support must also be provided to farmers and fisherfolks on sustainable management of feedstocks.

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Conflict of interest

The authors declare that they have no known competing financial interests or affiliations that could have appeared to influence the work reported in this book chapter.

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