

MMSU Hydrous Bio-ethanol (MMSU95hBE) III:
Development of Adaptable Technologies for Village-Scale Bio-ethanol Production

S. C. Agrupis¹, N.Mateo¹, M.C. Birginias¹, M. P. Lucas¹,
J.P Madigal, and F. Abenes²

Mariano Marcos State University¹ and Professor Emeritus, CalyPoly University,
Pomona CA, USA, DOST-Balik Scientist , US Fulbright Senior Fellow
and Affiliate Professor at MMSU²

ABSTRACT

The paper under review is a part of a big project at MMSU that embarks the production, testing and evaluation of hydrous ethanol as biofuel. MMSU Hydrous Bio-ethanol I (2010-2011) provided information on the quick production protocol, characterization, and testing of hydrous ethanol-gasohol blend (*MMSUhBE20*) as biofuel. Part II (2012-2013) focused on upscale production and performance of the different hydrous ethanol-gasoline blends from 20-90% mixture using spark ignition engines. Part IV (2013-2014) in a separate paper, dealt with the long term performance of spark ignition engines fueled exclusively with *MMSUhBE20*.

This paper, Part III (2013-2014), reports the improved and optimized fermentation and distillation protocols using sweet sorghum as feedstock. Fermentation parameters like sugar concentration, yeast activation time and temperature, fermentation period among others were optimized at the village scale. One hr activation of yeast under aerobic and ambient conditions afforded 76-82.34% fermentation efficiency after 72 hrs fermentation period. Elevating the activation temperature to 30-32°C in 30 mins improved the fermentation efficiency to 85%.

The improved reflux distillation system was 97-100% efficient in recovering the ethanol from the fermented sweet sorghum and sugar cane. Unlike the previous designs, the reflux kettle and reflux tower are equipped with digital temperature gauges and pressure valves for safety operation. The condenser is cooled with a circulating water from the cooling tower, hence zero water wastage. The furnace was improved at much reduced fuel wood input due to shortened distillation time. Ethanol output from the condenser is totally liquefied and cold. The most significant improvement of the new design is its high efficiency in recovering 95% pure ethanol from the beer skipping much time and energy for second distillation. Depending on the concentration of ethanol in the beer, the previous distillation system could only recover few liters of 95% ethanol and the rest have purity ranging from 81-93%, hence necessary for a second distillation to obtain an azeotrope fuel grade (95%) ethanol.

The facility can process bioethanol from different feedstock including palm juices. Noteworthy, is the cost effectiveness of the distillation facility when it was used to purify ethanol from other feedstock like the naturally fermented nipa sap. Even at lowest ethanol concentration of 5-6% v/v in the beer, it could recover the ethanol at 93% efficiency. For beer with higher ethanol concentration, the system could recover 98% azeotrope ethanol leaving only 2% of the total ethanol distillate for second distillation. The present technology costs PhP 52.43 and PhP 39.86 per liter hydrous ethanol from sweet sorghum and nipa sap, respectively,

The highlight of the study is the adaptation and pilot deployment of the developed fermentation and distillation technologies using nipa sap as feedstock. This is in collaboration with PhilRice in line with their fossil fuel free farming program.

Keywords: bioethanol, biofuel, hydrous bioethanol fuel, nipa sap

INTRODUCTION

The Philippine government considers the use of biofuels as one of the key ways to reduce carbon dioxide emissions and lessen the country's dependence on foreign oil. Republic Act 9637 (2006 Philippine Biofuels Act), mandates the use of 5% ethanol in gasoline by the year 2009 and 10% by 2011. Under the Act, the Philippine National Standards (PNS) specified that the ethanol used in blending should be 99.6% anhydrous. The technical requirements to produce anhydrous ethanol effectively cut out the participation of village-scale industries – the very sector that the legislation purportedly wants to benefit.

Hydrous ethanol (also known as azeotropic ethanol) is the most concentrated grade of ethanol that can be produced by simple distillation, without the further dehydration step necessary to produce anhydrous (or dry) ethanol. Both Hydrous and Anhydrous ethanol have been used as fuel (Wagner et al., 2009). Hydrous ethanol azeotrope exists as 95% ethanol-5% water and can be used as pure (“neat”) fuel in engines while anhydrous ethanol is currently used in fuel blends ranging from E-5 to E-85 (Karpov 2007). The process of dehydration is costly and energy-consuming. Studies have noted that hydrous ethanol is up to 30% less expensive than anhydrous ethanol; it is easier to produce and to handle; and it offers a better life cycle emissions profile than anhydrous ethanol.

The hydrous ethanol- azeotrope exists as 95% ethanol-5% water and the reasoning why it can not be identified as gasoline blend is the phase separation problem when mixed with gasoline. Indeed, under temperature lower than 15.56°C (60°F), previous works show that hydrous ethanol exhibit phase separation that makes it not suitable for fuel application. This could be true to countries with an annual average temperature lower than 15.56°C but not in the Philippines with an average annual temperature of 26.67°C (80°F) that even in the coolest month, the temperature does not fall below 25°C. Studies proved that water tolerance of ethanol/gasoline mixtures increases with increasing temperature that qualifies the Philippines as a potential user of hydrous ethanol-gasoline blends for mobility fuel.

Another negative drawback that confronts the use of hydrous ethanol as biofuel blend, is the belief that it contributes to rust formation in fuel lines of the stationary and mobile engines. The results of the rigorous testing of the 20% hydrous ethanol-gasoline

blend in spark ignition engines will be reported in a separate paper. It can be mentioned here, however, that our results demonstrate the feasibility of using hydrous ethanol instead of anhydrous. Our results confirmed that hydrous ethanol can be splash-blended effectively with gasoline without phase separation or other problems. Tests conducted by the authorized service center of the maker of our EFI test car confirmed the benefits of oxygenation and normal engine performance without sign of rust formation in the fuel lines and other associated parts of the engine.

Production of hydrous ethanol (90-96% % purity) followed exactly the same fermentation techniques in producing anhydrous ethanol (99.6% and above purity) which include fermentation, distillation and purification (further dehydration). However, techniques to improve ethanol yield at a given time varies under different conditions and feedstock and this often determines the competitiveness of the process and commercial viability of the technology.

At MMSU, our previous quick and dirty fermentation experiments used ordinary baker's yeast to ferment four different first generation feedstock namely, sugarcane molasses, sweet sorghum syrup and jaggery, and the Ilocano "basi" from sugarcane. With few modifications from the existing fermentation techniques, our proof of concept experiments under ambient conditions gave 76-82.34% sugar conversion efficiency in as little as 18-24 hrs giving ethanol yield of 12-13% (v/v) that is close to the maximum ethanol tolerable limit (15%v/v) of yeast.

The reflux distillation of the fermented hydrolysate gave ethanol recovery as high as 95-100% with ethanol purity of 89-95%. Ethanol collected with less than 95% purity were redistilled to attain azeotropic hydrous ethanol purity. Initial tests on the chemical, physical and mechanical properties of the hydrous ethanol and its gasohol biofuel formulations indicated the high potential of the product as biofuel. The hydrous ethanol was tagged as *MMSU 95 hBE* while its gasohol biofuel blend at 20% hydrous ethanol was named as *MMSU hBE20*.

Cognizant of the added cost of producing anhydrous ethanol, technical advantage of hydrous ethanol as biofuel blend, and our desire to develop adaptable and adoptable technologies at the village level, our group persists to continue optimizing our

production protocols for the production of hydrous ethanol at the village level. In so doing, ordinary ethanol feedstock growers can participate in this nascent biofuel industry.

OBJECTIVE OF THE STUDY

The overall objective of the study was to develop adaptable and adoptable technologies for the production of bioethanol at the village level. Specifically, the study aimed to: 1) improve fermentation conditions (time and temperature) for optimum yeast activation and fermentation efficiency; 2) develop appropriate process to recover and re-ferment residual sugar after fermentation; 3) improve design of the distillation facility for a cost-efficient ethanol recovery and optimal safety operation; 4) explore the adaptability of the fermentation and distillation protocol to nipa sap in search for an additional and more sustainable feedstock for bio-ethanol production; and 5) to determine the cost of producing hydrous ethanol

REVIEW OF LITERATURE

The signing of the Biofuel Act of 2006 in January 2007 made the Philippines the first country in Southeast Asia to have biofuel legislation in place. The lead agency responsible for the Philippine Biofuels Program is the Department of Energy (DOE). The DOE's energy strategy for the country is outlined in the Philippine Energy Plan 2012-2030 (PEP 2012-30) and National Biofuels Plan (NBP 2013-2030). The PEP 2012-2030 reflects the Philippine government's (GPH) mission to ensure the delivery of secure, sustainable, sufficient, affordable and environment-friendly energy to all economic sectors. The NBP 2013-2030, on the other hand, is a preliminary assessment of the previous National Biofuels Program for the period 2007-2012 (NBP 2007-2012), and outlines the short-, medium- and long-term plans of the National Biofuels Board (NBB). The NBB is chaired by the DOE. Both the PEP and the NBP are often reviewed and assumptions adjusted and revised. Of all the well structured policy making bodies for the biofuel industry, compliance with the current mandated 10% ethanol-gasoline blend, according to 2013 GAIN Report, continues to be unmet due to the inadequate capacity and competitiveness of existing ethanol distilleries.

According to the 2013 Global Agricultural Information Network (GAIN) Report, Philippines' four ethanol refineries have a combined annual capacity of 133 MI, but

produced just 16 Ml in 2012, roughly 6% of total ethanol consumption. Despite the incentives offered to potential biofuel (and RE) investors and an assured market, investments have been inadequate. Although the country is a major sugarcane producer, low productivity and high production costs erode the competitiveness of locally grown sugarcane. Local average sugarcane production of 60 tons/hectare is one of the lowest in Asia. These competitive challenges are compounded by trade liberalization commitments under existing regional free trade agreements, specifically, the ASEAN-FTA or AFTA. Under the AFTA, Philippine tariffs on sugar will go from 18% in 2013 to 5% in 2015. As a result, imported ethanol is expected to satisfy the gap between local production and mandated blend requirements (2013 GAIN; DOE-REMB 2013). Given the resources of the country, it is feared that having then become the biggest importer of rice; the country will also become just as famous as the biggest importer of ethanol.

Ethanol is globally advocated as a viable alternative either as oxygenate to gasoline fuel (Wagner et al., 1979) or as neat fuel. As automotive fuel, it can be used alone in specially designed engines, or blended with gasoline and used with little or no engine modifications (Faiij et al., 2008). Motorboats, motorcycles, lawnmowers, chain saws, etc. can all utilize the cleaner gasoline/ethanol fuel. Most importantly, the millions of automobiles on the road today can use this improved fuel. Vehicle owners all over the world use ethanol blends exclusively with no performance problems. In some older carburetor-type vehicles, adjustments may be required for the air intake. Ethanol has many advantages as an automotive fuel. In spark ignition engines, ethanol emits significantly less carbon monoxide and air toxic pollution than gasoline, and therefore reduces the amount of harmful emissions released into the atmosphere (Karpov, 2007).

Bioethanol made from agricultural crops "breathe" carbon dioxide and gives off oxygen. This maintains the balance of carbon dioxide in the atmosphere. Increased use of renewable fuels like ethanol help counter the pollution and global warming effects of burning gasoline. Hydrous ethanol is the most concentrated grade of ethanol that can be produced by simple distillation. Also known as azeotropic ethanol, it exists as 95% ethanol-5% water. Dehydration of hydrous ethanol to its anhydrous form requires the use of more sophisticated distillation processes, membrane filtration, or molecular sieves; processes that are expensive and beyond the capabilities of ordinary ethanol producers. Anhydrous ethanol is up to 30% more expensive to produce than hydrous ethanol, which

is also easier to handle. Most importantly, hydrous ethanol offers a better life cycle emissions profile than anhydrous ethanol.

Fuel ethanol blends are called "gasohol," the most common blend being 10% anhydrous ethanol mixed with 90% gasoline (E10). In the Philippines, this blend is mandated by the 2006 Biofuels Law (Orculo, 2007). Because ethanol is a high-octane fuel (2.5 - 3 points above the octane of gasoline), with high oxygen content (35% oxygen by weight); it allows engines to more completely combust the fuel, resulting in fewer emissions.

In some countries, hydrous ethanol is used along with anhydrous to fuel motor vehicles. In countries like Brazil, hydrous ethanol is used as 100% ("neat") fuel while anhydrous ethanol is used in flex fuel blends ranging from 5% (E-5) all the way up to 85% (E-85) (Karpov, 2007). Hydrous ethanol gasohol blends, however, cannot be used at temperatures lower than 15.6°C (60°F) because the mixture can exhibit phase separation, rendering such blends unsuitable for fuel use (Mills & Ecklund, 1987). This explains why in countries where temperatures vary widely from summer to winter, (e.g. North American countries and Europe), only anhydrous ethanol is used as oxygenate and in gasohol blends. If ever hydrous ethanol is used, expensive additives and dispersants are necessary to prevent phase separation, negating the cost advantage of using the azeotrope. When coupled with reformulations that are mandated during summer and winter months, the use of hydrous ethanol is rendered impractical in most countries with cold climates.

Such is not the case in the Philippines. With an average annual temperature of 26.7°C (80°F), even the coolest months do not register temperatures below 18.3°C. Several empirical studies have established that water tolerance of ethanol-gasoline mixtures improves with increasing temperature (Korotney, 1995). This suggested to us, the possibility that hydrous ethanol-gasoline blends can be used successfully in the Philippines without the need for additives or dispersants.

Production of hydrous ethanol (90-96% % purity) followed exactly the same fermentation techniques in producing anhydrous ethanol (99.6% and above purity) which include fermentation, distillation and purification (further dehydration). However, techniques to improve ethanol yield at a given time varies under different conditions and

feedstocks and this often determines the competitiveness of the process and commercial viability of the technology.

Generally, yeasts start the fermentation process in 24 hrs but producing ethanol to its maximum tolerable limit of 15% (v/v) usually lasts from 48 hrs to 3 months. The engineered yeast developed by group of scientists in Whitehead Institute and MIT in the US completes fermentation in 21 hr. Primarily, fermentation process produces hydrous ethanol and removing water from the system to a certain extent is accomplish by distillation. Reflux still is one of the distillation techniques. Reflux still is a facility that allows the distillate vapors from a boiler to rise up a column to the top where the vapors are condensed. The condensed liquid is then allowed to run back down through the rising vapors to a point where the temperatures become hot enough that it boils again. This process is called refluxing. As this cycle continues, the mixture inside the tower is effectively re-distilled. In the process, the components of the mixture separate into discrete layers within the column based on their boiling points. At 78.1°C, ethanol at 95% (azeotrope-ethanol) purity is collected and cannot be further distilled to obtain a higher purity. To obtain a higher concentration of ethanol, the azeotrope must be broken using a retrainner such as Benzene or cyclic Hexane, to create a ternary azeotrope that can be distilled off to leave pure ethanol. Alternatively, the use of dessicants such as calcium oxide or molecular sieves such as zeolites and membrane filtration may be used to increase the ethanol concentration. All of these methods increase the cost of producing the desired gasohol blend to as much as 30%.

As we develop mechanisms for technology transfer for the production and use of hydrous ethanol either as gasoline blend or as feedstock for anhydrous ethanol, we are challenged by sustainability issues specifically on reliable feedstock supplies and local government support. The main fuel crops for ethanol in the Philippines are sweet sorghum and sugar cane. However, these crops compete with the land requirements of the Philippines' main food crops like rice and corn. For this reason, the group is refocusing its efforts in exploring other sustainable feedstock that do not create issues on food vs fuel. Nipa palm (*Nypa fruticans*) is the most promising of these feedstock. It has more advantages over other fuel crops in all aspects. First, it does not have to compete with food crops for land and water resources because it grows where most crops can not grow and it branch dichotomously; second, it requires very little maintenance because

once established, it will last for at least 50 years (in contrast with all other sources of bioethanol that need to be replanted after harvest; third, it has many other uses and fits in such innovative systems as aquasilviculture designed to rehabilitate abandoned fishponds where fishery and nipa production compliment each other.

Nipa, is an indigenous palm species native to the coastlines and estuarine habitats throughout the country. Aside from its popularity as material for “bahay kubo” (native thatched hut), it also produces sap that contains 13 to 15° Brix sugars. To harvest this sugar, nipa flower clusters are tapped before they bloom using open bamboo vessels that allow continuous aerobic fermentation starting from the first drop until emptied into open containers every 24 hours. This fermented sap yields a sweet, potable alcoholic beverage called “tuba” with ethanol concentration ranging from 2 to 3% ethanol. It is hypothesized that by limiting the period of aerobic fermentation, ethanol concentration in tubacan be increased, a crucial requirement if nipa sap is to be exploited as a source of fuel grade ethanol. There is already an established industry producing low grade alcohol (40-45%) beverages from Nipa in communities where Nipa palm plants abound with full local government support. Our preliminary experiments showed adaptability of nipa sap to the propriety protocols develop by the MMSU Hydrous Ethanol Team yielding ethanol purity as high as 95-96%. This new initiative of MMSU is in partnership with Philippine Rice Research Institute's in support to one of the Institutes’s flagship program – fossil-fuel free rice farming.

MATERIALS AND METHODS

Improvement of fermentation conditions for optimum yeast activation and fermentation efficiency

Yeast activation time and working temperature. Previous lab scale fermentation experiments used 4-6 hr aerobic activation periods before yeasts were pitched into anaerobic fermentation vessels. Under ambient conditions, the set up gave 72-76 % ethanol conversion efficiency in as little as 18-24 hrs. Succeeding experiments lowered the activation period to 1 hr which improved fermentation efficiency to 85 %. The present trial explored the fermentation efficiency of yeast activated to 30 and 60 mins. Two working conditions were evaluated: one was under room temperature (27-28°C) and the other was under elevated temperature at 30-32°C.

Known amount of yeast was activated in a known volume of feedstock withdrawn from the fermentation vessel. Separate containers containing the feedstock and the propagating yeast were continuously stirred at room temperature and elevated temperature for 30 and 60 min before they were pitched into the separate fermentation vessels. The fermentation vessels were installed with a breather and a provision for mechanical stirring to maintain anaerobic conditions. The experiment was conducted twice.

Recovery and re-fermentation of sugar residue after distillation

One of the drawbacks of using commercial Baker's yeast is its high sugar requirement for optimum activity. A preliminary lab scale experiment showed optimum activity occurs at 30% sugar concentration, giving ethanol yield of 12-14% (v/v) which is close to the maximum ethanol tolerable limit (15%v/v) for yeast viability. Given such limitation on yeast viability, it is expected that considerable amount of sugar approximately less than half the original concentration are not fermented. The objective of this experiment was to evaluate the recovery and re-fermentability of the sugar residue after distillation.

Two trials were evaluated. Trial 1 involved the addition of fresh sugar to the sugar residue to attain an initial 30% concentration. Trial 2 involved concentrating the sugar residue to 30% by boiling off excess water. Both sugar feedstock were separately added with known amount of yeast using the fermentation protocol followed in the previous set up.

Design improvement of the distillation facility for optimal efficiency and safety operation

Safety operation. Previous design of the reflux distillation system did not warrant safety operation. Two separate circumstances- blowing out of the reflux tower lead us to re design the distiller in order to monitor temperature and pressure accurately. Hydro-testing was also conducted to the reflux kettle and condensers to assure that no possible leak happen during the distillation process. Instrumentation and control was installed to include safety relief valve and thermo controllers that may give alarm sound when critical set temperature is reached. Other added safety feature is the furnace that contains the combustion inside the furnace compared to the previous designs that employs an open fire during the distillation process.

Improvement of cooling tower for zero water wastage. Like any distillation system, water supply is the life of the condensation process. In conventional systems, water is continuously lost during distillation, which is costly, wasteful and sometimes harmful to the environment. The objective of this experiment was to improve the design of the cooling and water recycling system to attain a zero-water loss distillation protocol. Prior this design under evaluation, there have been several innovations to address the zero-water wastage. Under ambient conditions, the system recycles water and maintain the coolness of the circulating water for optimum condensation of the ethanol vapor. One negative drawback of the previous designs is the inability of the cooling water to condense all the ethanol vapor. Moreover, ethanol distillate coming out of the outlet is hot, hence lost of ethanol through evaporation is inevitable. The present design adapts the natural draft cooling tower design where circulating water to the condenser are naturally cooled down. Temperature is maintained at slightly higher than the ambient room temperature. The said cooling tower was also designed mobile and can easily be assembled and disassembled for convenient installation and maintenance purposes.

Improvement of the condenser unit for optimal ethanol recovery. Previous condenser designs in addition to the reflux column condenser utilized a three stage-single line condensers arranged after the other totaling a length of about 4 meters. In contrast, the present design involve a U-tube counter flow design with a total length of only 1.2 meter which can easily be opened for maintenance purposes.

Design improvement of the furnace for much reduce energy input. Previous design of the furnace was made of concrete and permanent. The present design is made up of MS plate with brick clay. The devise was made mobile, smaller than the previous, and installed with asbestos materials to conserve and contain the heat inside the system. A small blower was installed to allow an even distribution of heat in the system.

Adaptability of the fermentation and distillation protocol to other feedstock like nipasap

Sustainability issues on feedstock is one of the most important concern in the biofuel industry because of the global debate on food vs fuel. To address this, other feedstock were explored and the adaptability of the fermentation and distillation protocol develop for sweet sorghum and sugarcane were evaluated using other feedstock. Among the most potential one is Nipa (*Nypa fruticans*) which sap contains 13 to 15° Brix sugars. The plantation is stable, grows in the swamp areas, it is perennial and grows for more than 50 years once established. The nipa sap is naturally fermenting and most plantation stand are established for shikel and low grade wine production. We hypothesized that by limiting the period of aerobic fermentation, we can increase the concentration of ethanol in tuba, a crucial requirement if nipa sap is to be exploited as a source of fuel grade ethanol. An experiment comparing the yield of ethanol under aerobic and anaerobic storage for periods ranging from 1 to 8 days prior to distillation were conducted at the MMSU Bioethanol Laboratory and on site at a Nipa plantation in Pamplona, Cagayan. Nipa sap were collected in the traditional manner. Half of the sap samples were kept in traditional open containers while half were stored in containers fitted with breathers that allow gas to escape but prevent air from going in (anaerobic). Ethanol was recovered quantitatively using the 13L reflux distiller. At the village scale, naturally fermented nipa sap and low ethanol grade wine “lambanog” with 5 to 6% v/v and 18-20% v/v ethanol concentration, respectively were distilled using the optimized village scale reflux distiller(Design 5).

RESULTS AND DISCUSSION

Improvement of the working conditions for optimum yeast activation and fermentation efficiency

To start the fermentation process, it is important that the yeast must first be activated. To do this, the yeast is introduced to a favorable liquid medium which is most often the same feedstock as in the fermentation medium to encourage rapid activation prior to adding to the hydrolysate. Once the yeast culture has propagated to a desired density, it is pitched into the hydrolysate to start the anaerobic fermentation process. This method is preferable to adding the yeast directly, for several reasons. First and foremost, it results in a more rapid fermentation, as the yeasts have already grown and multiplied and are now ready for anaerobic fermentation. The sooner the yeast can get to work, the

better the resulting fermentation will be. Activating the yeast can save considerable time to complete the entire fermentation process as well as increase the ethanol concentration. Secondly, it ensures viability of the yeast. Normally, when you use yeast, you have no idea on its viability and effectiveness. By making a starter solution before pitching, we can discover whether yeast is viable or non-viable.

Thirdly, a starter properly made will acclimate the yeast to its destined environment. When the starter is acclimated, it will practically explode with activity once added to the primary and do what nature and selection has programmed it to do with much more efficiency. Activation takes valuable time, however; and in a commercial situation, it is important to identify the minimum time required to get satisfactory fermentation results. Our experiments have indicated that an activation period of as little as 1hr is effective enough to give 83.47% efficiency; reducing this time further to 30 minutes results in a reduction of fermentation efficiency (79.57%) as shown in Table 1.

Table 1. Average fermentation efficiency (%) of *S. cerevisiae* at two different activation periods under laboratory and upscale condition.

Activation period, min	Under Room condition, 27-28°C		Under elevated temp, 30-32°C
	(a) Laboratory, 10L	(b) Upscale, 149L	(c) Upscale, 140L
30	85.85	79.57	85.20
60	85.17	83.47	85.00



Fig. 1. Fermentation set up at laboratory (a) and Upscale condition (b) and (c)

Recovery and re-fermentation of sugar residue after distillation

Even under optimum conditions, there are considerable sugars that remain after fermentation and distillation. Attempts to utilize these residual sugars by simply adding yeast gave very poor results. Our experiments (Table 2) centered on adjusting the residual sugar concentration to the optimum 30% by either adding fresh sugar or concentrating the sugar by boiling out the water in the hydrolysate. Results indicate that the addition of fresh sugar is more effective than simply boiling out the water to achieve the optimum sugar concentration. After 2nd cycle fermentation, virtually all of the added sugar in Trial 1 was converted into ethanol (97.43%) whereas only half of the remaining sugars in the re-concentrated are converted to ethanol (47.26%). This is likely due to anti-yeast nutritive factors that are produced in the initial fermentation process or that some of the remaining sugars have simply become non-fermentable. At any rate, our findings indicate that there is still value in the residual sugars for a second fermentation as the addition of fresh sugar can result in much higher fermentation efficiency.

Table 2. Ethanol potential of residual sugar after fermentation and distillation.

Experimental Trials	Brix of Sugar Residue in Hydrolysate after Distillation, %	Final vol. of sugar feedstock for fermentation, L	Computed 95% ETOH yield,L	Actual ETOH yield,L	ETOH Conversion Efficiency, %
Trial 1- fresh sugar added to sugar residue to make 30% Brix	15	12	1.93	1.89	97.93
Trial 2- sugar residue concentrated to make 30% Brix	16	12.5	2.01	0.95	47.26

Design Improvement and Optimization of the Distillation Facilities for Optimal Safety Operation and Efficiency

Distillation is the most widely used separation technique in bioethanol production. One disadvantage of the distillation process is the large energy requirement, accounting for around 25-40% of the total energy usage. Distillation consumes a great deal of energy for providing heat to change liquid to vapor and large amounts of cool water to condense the vapor back to liquid at the condenser.

Clearly, the energy requirements for ethanol production must be reduced markedly to make it a competitive fuel. This can only be done by a variety of technology and plant design improvements. Distillation columns are used for about 95% of liquid separations and the energy use from this process accounts for an estimated 3% of the world energy consumption (Hewitt et al, 1999). With rising energy awareness and growing environmental concerns there is a need to improve the design and operation of distillation systems to reduce overall plant energy consumption and operating costs.

Design Improvement and Optimization of the Distillation Facility

Our group has succeeded in designing and improving a distillation system that utilizes a much smaller amount of energy and water. Table 3 shows the comparative performance of the different designs of the distillation system whiel Fig 2-6 shows the distillation facilities. Cost effectiveness of the designs was measured based on the mass of fuel wood and volume of water used to produce a liter of ethanol, and the efficiency

of the system to recover directly the fuel grade 95% ethanol. Computation of the mass of fuel and volume of water was based on the aggregate volume of collected ethanol which was computed based on the concentration of ethanol. Distillation stopped when the temperature in the reflux tower signals to 85°C. Concentration of the collected distillate ranges from 81-93% which make it necessary to subject the distillate to 2nd distillation. This is an added input to the production cost, hence need to be addressed. Design 5 (Fig 6) gave the lowest firewood input of 1.79 kg wood/L ethanol. In terms of water usage, Designs 1 and 2 (Figs 2-3) used running water throughout the distillation process, hence higher water usage of 0.18 and 0.15 m³/L respectively. Design 3 (Fig 4) was equipped with recycling water system using a plastic container filled with 200 L water. Since volume was too small, the circulating water in the reservoir easily warmed up. Coolness was maintained by addition of ice blocks. The system could only recover 4.8% azeotrope ethanol from the total ethanol collected. Ninety two percent of the total distillate has ethanol purity of 81-93% which must be subjected to second distillation. Water recycling system in Design 4 (Fig 5) was improved. It involve two stage water reservoir and the circulating water is cooled with an installed radiator in the system. Recovery of 95% ethanol was 61% of the total distillate collected. Design 5 (Fig. 6) is the most improved system. The circulating water is cooled naturally in the cooling tower. Recovery of 95% ethanol is 93.25% efficient, skipping most of the second stage distillation.

Table 3. Comparative performance of the different designs of the distillation system for the production of hydrous ethanol.

Designs	Mass of fuel wood used/L ETOH, kg/L ETOH	Vol. H ₂ O used/L ETOH, m ³ /L ETOH	Distillation rate, L/hr	Time to finish distillation, hr	Efficiency of recovering 95% ETOH directly
Design 1 -upscale manufacturer's prototype with running water	4.09	0.18	2.28	8	4.8
Design 2 - Improved Design 1 with insulator and running water	3.20	0.15	2.29	7	13.35
Design 3 - Improved Design 1 with recycling water system	4.09	0.009	2.28	8	4.8

Design 4- Based on Design 1 with improved furnace and with recycling water system equipped radiator to cool the water	1.86	0.05	2.88	7	61
Design 5- Based on Design 1 with improved furnace and natural draft cooling tower and water recycling system	1.79	0.072	2.60	4	93.25

Legend: Volume of fermented beer for distillation: Designs 1-3 was 185L; Designs 4-135L; Design 5-100L



Fig. 2 . Design 1. 241L -upscale manufacturer's prototype.

Fig. 3. Design 2. 241L -upscale manufacturer's prototype with insulator.

Fig. 4. Design 3. 241L -upscale manufacturer's prototype with modified cooling system.

Fig. 5. Design 4. 150 L capacity , improved furnace and cooling system(MMSU-based CLSU design)

Fig. 6. Design 5. 200L capacity, improved furnace and cooling system

The advantages of water recycling are obvious. For one, it prevents waste of a precious natural resource particularly in those places where natural water supply is scarce and drinking water is not even enough to meet the human demand. Secondly, this system is not dependent on tap water supply for cooling the condenser unit as, in the case of MMSU and most areas of the Philippines, tap water supply may not be available regularly. Lastly, during summers, water coming from the tap can be very hot and may fail to effectively cool the condenser and reduce the speed of distillation. Based from the above criteria, Design 5 is the most ideal distillation system. It gave the lowest fuelwood consumption, most efficient water cooling system, and gave the highest efficiency in recovering 95% ethanol.

Unique Features of Design 5 (Fig 6) for Optimal Safety Operation

Safety operation. Previous design of the reflux distillation system did not warrant safety operation. Two separate circumstances- blowing out of the reflux tower lead us to re design the distiller in order to monitor temperature and pressure accurately. Hydro-testing was also conducted to the reflux kettle and condensers to assure that no possible leak happen during the distillation process. Instrumentation and control was installed to include safety relief valve and thermo controllers that may give alarm sound when critical set temperature is reached. Other added safety feature is the furnace that contains the combustion inside the furnace compared to the previous designs that employs an open fire during the distillation process.

To address this, an automated digital thermometer were installed both at the reflux kettle and reflux tower. The thermometer at the reflux kettle was set to optimum temperature of 100°C while 78-80°C at the reflux tower. A safety pressure release valve was installed for optimum safety. Unlike the previous design, the reflux tower was safely sealed to avoid blowing up when pressure exceeds the maximum pressure limit.

Improvement of cooling tower for zero water wastage. Like any distillation system, water supply is the life of the condensation process. In conventional systems, water is continuously lost during distillation, which is costly, wasteful and sometimes harmful to the environment. The objective of this experiment was to improve the design of the cooling and water recycling system to attain a zero-water loss distillation protocol. Prior this design under evaluation, there have been several innovations to address the

zero-water wastage. Under ambient conditions, the system recycles water and maintain the coolness of the circulating water for optimum condensation of the ethanol vapor. One negative drawback of the previous designs is the inability of the cooling water to condense all the ethanol vapor. Moreover, ethanol distillate coming out of the outlet is hot, hence lost of ethanol through evaporation is inevitable. The optimized design adapts the natural draft cooling tower design where circulating water to the condenser are naturally cooled down. Temperature is maintained at slightly higher than the ambient room temperature. The said cooling tower was also designed mobile and can easily be assembled and disassembled for convenient installation and maintenance purposes.

Improvement of the condenser unit for optimal ethanol recovery. Previous condenser designs in addition to the reflux column condenser utilized a three stage-single line condensers arranged after the other totaling a length of about 4 meters. In contrast, the optimized design involve a U-tube counter flow design with a total length of only 1.2 meter which can easily be opened for maintenance purposes.

Design improvement of the furnace for much reduce energy input. Previous design of the furnace was made of concrete and permanent. The optimized design is made up of MS plate with brick clay. The device was made mobile, smaller than the previous, and installed with asbestos materials to conserve and contain the heat inside the system. A small blower was installed to allow an even distribution of heat in the system.

Adaptability of the Fermentation and Distillation Technologies Using Nipa Sap as Feedstock

As we develop mechanisms for technology transfer and advocacy on the production and use of hydrous ethanol as biofuel, we are challenged by sustainability issues specifically on reliable feedstock supplies and local government support. The main fuel crops for ethanol in the Philippines are sweet sorghum and sugar cane. However, these crops compete with the land requirements of the Philippines' main food crops like rice and corn. Hence, we endeavor to expand the adaptability of our technologies using other feedstock that do not potentially create issues on food vs fuel. Nipa palm (*Nipa fruticans*) is most promising. It has many advantages over other fuel crops in all aspects. First, it does not have to compete with food crops for land and water resources because it grows where most crops can not grow; second, it requires very little maintenance

because once established, it will last for at least 50 years (in contrast with all other sources of bioethanol that need to be replanted after harvest); third, it has many other uses and fits in such innovative systems as aquasilviculture designed to rehabilitate abandoned fishponds where fishery and nipa production compliment each other. In addition, using traditional fermentation protocols, there is already an established industry producing low grade alcohol (40-45%) beverages from Nipa in most communities where nipa palm plants abound. Our preliminary experiments showed adaptability of nipa sap to MMSU propriety fermentation and distillation protocols yielding ethanol to a purity as high as 92-95%. This new initiative is in partnership with PhilRice Research Institute's flagship program – fossil-fuel free rice farming.

Fermentation protocol. Table 4 shows the ethanol concentration (% v/v) of nipa sap fermented under strictly aerobic and facultative anaerobic conditions. Results indicate that fermented sap stored under anaerobic gave higher ethanol concentration than those subjected under aerobic conditions both at ex-situ and in-situ environment. After 8 days, fermented sap kept in open containers lost almost all its initial ethanol (0.75%) while those kept under anaerobic conditions remained at 4.74% in ex-situ conditions. Under in-situ environment, ethanol was not reduced as drastically as in ex-situ but lower than anaerobic. We conclude that simply changing the storage conditions after harvesting the fermented sap can increase the yield of ethanol by as much as 33%. Further increase in ethanol yield may be achieved by controlling yeast activity during the collection process.

Table 4. Ethanol concentration (% v/v) of Nipa Sap fermented under Strictly Aerobic and Facultative Anaerobic conditions.

Observation Time, day	Ethanol concentration, % v/v on fermented sap				
	<i>Ex-situ</i> condition		Observation Time, day	<i>In-situ</i> condition	
	Strictly Aerobic	Facultative Anaerobic		Strictly Aerobic	Facultative Anaerobic
1	2.91	2.98	1	3.34	4.80
2	2.98	3.27	2	4.60	5.66
4	2.98	3.84	3	5.27	5.43
8	0.75	4.74	5	4.66	5.47

Distillation protocol. The adaptability of the system with nipa sap was tried at upscale condition in comparison with sweet sorghum. The result in Table 5 showed the adaptability of the distillation facilities with nipa sap (Table 5). The data shows that even at lowest ethanol concentration of 5-6% v/v in the beer, it could recover the ethanol at 93% efficiency. For beer with higher ethanol concentration, the system could recover

98% azeotrope ethanol leaving only 2% of the total ethanol distillate for second distillation. The distillation process of 100L fermented nipa sap was completed in 3 hrs. Higher concentration of ethanol in the beer makes the distillation system more cost-effective.

Table 5. Performance of Design5 reflux distillation system using sweet sorghum and nipa sap beer.

Distillation Parameters	Feedstock		
	Nipa Trials		Sweet Sorghum Trials
Volume beer, L	100	100	100
Conc of ETOH in the beer, % v/v	19	5.5	12.7
Vol. 95% ETOH, L	17	5	13.5
Vol. lower grade ETOH, (87-89%)	3	0.4	1
Total Yield 100% ETOH, L	18.76	5.10	13.24
Processing time, hr	6	3	5.35
Distillation efficiency to collect 95% ETOH, %	98.74	92.72	98.07

Adaptation and Pilot Deployment of MMSU95hBE Production Technologies

One of the main goals of our project is to develop processing technologies that are ADAPTABLE and ADOPTABLE at the village level to capacitate producers of feedstock to also become fermenters, distillers, and dealers of the oxygenate and biofuel. The developed village-scale bioethanol production facilities using nipa as feedstock were adapted and deployed successfully in Cabaggan, Pamplona Cagayan in partnership with PhilRice for their Fossil-Fuel Free Farming Program. The facilities are now being used by the technology takers under our close supervision and evaluate the on-field adaptability of our fermentation and distillation technologies. As shown in Table 6, the three trials conducted by the farmer consistently show higher ethanol concentration in the beer (8% v/v) compared to the data obtained in Table 4 indicating the adaptability of the fermentation protocol (facultative anaerobic) in field and up-scale conditions. The efficiency of the distillation facilities to recover 95% Ethanol is lower than those obtained in Table 5. This is expected since the facility was just deployed on Oct 7. Farmers need more training in the operation of the facility specially in the firing and control of heat in the furnace. Training is scheduled before the year ends to further capacitate the farmers in the techno-how operation of the bioethanol facilities.

Table 6. On-field validation on the adaptability of the fermentation and distillation

protocols at village-scale.

Distillation Parameters	Farmer's Trial		
	12 Oct	16 Oct	20 Oct
Volume beer, L	160	160	160
Conc of ETOH in the beer, % v/v	8.13	8.21	8.72
Vol. 95% ETOH, L	11	12	10
Vol. lower grade ETOH, (87-92%)	3	2	5
Total Yield 100% ETOH, L	13.01	13.14	13.91
Distillation efficiency to collect 95% ETOH,%	84.60	91.32	71.89

With this big improvement in ethanol recovery at village-scale, there will be more facilities to be deployed next year under the USAID funding. Through this increasing awareness and support from different agencies, we hope to result in a wider participation of small-scale producers in rural communities for higher levels of vertical integration in the bioethanol industry i.e., instead of selling raw products such as juices to large bioethanol plants, farmers can profit from the sale of fuel-grade ethanol; generation of employment and alleviation of rural poverty through the development of village level bioethanol industry; maximization of the use of sustainable feedstock that do not create issues of food vs fuel; and reduction in the amounts of ethanol importation and contribute to the ethanol self-sufficiency goals of the country.

Economic Analysis of the Optimization Using Sweet Sorghum as Feedstock

The ultimate objective of the whole project is to optimize the production of hydrous ethanol in order to lower the cost to be competitive in the market considering the cost of fossil fuel. The economic analysis presented below is based on the improved 200L reflux distiller developed by MMSU (Table 6), comparing sweet sorghum and nipa sap. The sweet sorghum feedstock (jaggery) is priced at the least PhP25 per liter from the BAPAMIN Cooperative in the City of Batac, Ilocos Norte. The nipa as source of sap is a naturally growing mangrove plant, hence, there is no production cost accounted for.

The cost of sweet sorghum feedstock accounts more than 72% of the total cost of producing hydrous ethanol. Labor accounts only 18% while electricity and fuelwood a little higher than 2.85% of the total cost. The high cost of the feedstock is attributed to the long process in producing jaggery from extraction of the sweet sorghum juice to cooking. Accounting all the inputs (i.e., labor and materials) for the 200L capacity, the production cost per liter of hydrous ethanol amounted to PhP52.43 (fermentation to distillation). This amount is lower than the current pump price per liter of gasoline at

PhP54.00 which indicates a positive perspective for sweet sorghum as feedstock for village-scale. Note however, that further processing (dehydration) of the hydrous ethanol to anhydrous would entail about 20-30% more of the cost of production.

Interestingly, the project also explored the potential of nipa (*Nipa fruticans*) as feedstock for bioethanol. Nipa sap has naturally fermenting properties, hence, there is no cost of yeast and additives. This is a big savings on the production cost for bioethanol. Labor cost for sap collection and hauling to the processing site accounts 46.83% while electricity and fuelwood require about 11.14% of the total cost. The cost per liter ethanol is PhP39.86 far cheaper than that of sweet sorghum. This is a very encouraging result considering the comparative advantage of nipa relative to sweet sorghum.

These results would show that a village-scale production of bioethanol is economically viable using the fermentation and distillation protocols developed by MMSU. However, further validation of the results are on-going with the deployment of the facility under a PhilRice funded project specifically for nipa and for other feedstocks under a USAID-STRIDE project.

Table 6. Comparison on the cost of hydrous ethanol production using sweet sorghum and nipa sapat up-scale condition.

PARTICULARS			TOTAL COST (PhP)			
			Nipa Sap		Sweet Sorghum	
	Unit	Cost/Unit	Input (Qty)	Total Cost, PhP	Input (Qty)	Total Cost, PhP
A. FERMENTATION						
Volume beer, L			100		100	
Nipa sap, 15°Brix						
Sweet sorghum, 75° Brix	kg	25			20	500
Yeast 1 & 2	g	0.312 5	-	-	-	22.97
Additives	g	1.024	-	-	-	13.02
Total Cost			-	-		535.99
B. LABOR						
Sap Collection	PhP	31.35	4	125		
Sap Hauling	PhP	31.25	0.5	15.63		
Total Cost				140.63		
C. DISTILLATION						
Labor	Hr	31.25	4	125	4	125
Electricity	Kwh	9	1.5	13.5	1.5	13.5
Fuelwood	m ³	600	0.33	19.8	0.33	19.8
Total Cost	PhP			158.3		158.3
Total Cost A+B/A+C	PhP			298.93		694.29
Ethanol yield	L			7.5		13.25
Cost ETOH/L	PhP			39.86		52.43

CONCLUSION AND RECOMMENDATION

The present study- MMSU Hydrous Bio-ethanol III:Development of Adaptable Technologies for Village-Scale Bio-ethanol Production aimed to optimize the working conditions during fermentation, develop appropriate process to recover and re-ferment residual sugar after fermentation and distillation, improve design of the distillation facility for optimal ethanol recovery and safety operation, deploy facilities for on-field adaptation of the ethanol production technologies, and determine production cost of hydrous ethanol under village –scale. The results of the study warrant the fermentation and distillation technologies to be considered cost-effective protocol.

Optimum fermentation efficiency of yeast is best attained when activated under elevated temperature of 30-32°C for 30-60 mins. Design 5 of the reflux distillation system satisfies all the features that makes it more efficient than the previous designs. The features include safety operation controller/device, zero water wastage, reduced fuel wood input, and high efficiency in recovering 95% pure ethanol.

The optimization trials and studies have resulted in significant recommendations for the pilot deployment of the facilities. The present technology costs PhP 52.43 and PhP 39.86 per liter hydrous ethanol from sweet sorghum and nipa sap, respectively, the improved reflux distiller developed by MMSU is proven as an energy-efficient distillation facility for village-scale ethanol fuel production. With the optimization of the hydrous ethanol production from sweet sorghum, the high cost of the feedstock makes the production cost per liter expensive relative to that of nipa. Further efforts should be exerted to reduce the cost of sweet sorghum feedstock.

In partnership with PhilRice and LGU Pamplona, one unit of the optimized facilities was deployed using nipa as feedstock. This is in line with the fossil fuel free farming program of PhilRice. The ethanol product will be used to trial run their farm machineries purposely fabricated using ethanol as fuel. Other higher value ethanol-based consumer products will be explored and taught to local producers for added income.

Other potential feedstock for bioethanol should be explored and tested not only for their economic feasibility but social and environmental as well. For example, Nipa palm is a bio-energy crop that is widely available yet underutilized and thus deserves serious consideration as biofuel feedstock.

Under the PhilRice and USAID funding, we expect more deployment of the technology to actual village environment. Such development will help will us further validate the above results to come up with more realistic and conclusive results before recommending its economic viability for commercialization.

. REFERENCES

- Borromeo, B.B., R.R. Coloma, N.D. Domingo, and E.J.P. Tabunan. 2011. Performance Testing of Spark Ignition Engine Using Characterized Hydrous Ethanol Blends from Sweet Sorghum Feedstock. Undergraduate Research Study.College of Engineering.Mariano Marcos State University. City of Batac.120 pp.
- Costa, C. R., and Sodre, J.R., 2010. Hydrous Ethanol vs. Gasoline-ethanol blend: Engine Performance and Emissions. *Fuel* 2010; 89:287-293
- DOE. 2008. National Biofuels Action Plan
<http://www1.eere.energy.gov/bioenergy/pdfs/nbap.pdf> retrieved November 11,2013
- Domingo, N.D., J. A. Ignacio, F.J.D. Ariano, F.J.D, and N.P Yadao. 2013. Fabrication and Testing of an Electric Dynamometer for Stationary Engines.Undergraduate Research Study.College of Engineering.Mariano Marcos State University.City of Batac 2906.48 pp.
- Faaji, A., A.Szwarc and A. Walter. 2008. Demand for bioethanol for transport. In: Zuurbier, P and J van de Vooren, editors, *Sugar Cane: Contributions to ClimateChange*.Wageningen Academic Publishers, the Netherlands.
- Karpov, S. "Ethanol as a High-Octane, Environmentally Clean Component of Automotive Fuels." *Chemistry and Technology of Fuels and Oils* 43.5 (2007): 355-61.
- Korotney, D. 1995. Water Phase Separation in Oxygenated Gasoline. [Www. Epa.gov/OMS/regs/fuels/rfg/waterphs.pdf](http://www.epa.gov/OMS/regs/fuels/rfg/waterphs.pdf)
- Mills, G. A, and E.E. Ecklund. 1987. Alcohols as Components of Transportation Fuels. *Annual Review of Energy* 12: 47-80.
- Orcullo Jr. N.A. 2007. Biofuels Initiatives in the Philippines. De La Salle University-Dasmariñas.
- Wagner, T., D. Gray, B. Zarah, and A. Kozinski. 1979. Practicality of Alcohols as Motor Fuel.Tech. no. 790429. Chicago, Illinois: Amoco Fuels.
- Zanin, M.G. 2007.The Green Airport Concept and the International Flight Academy on Biofuels. Masters Thesis. Baylor University Institute for Air Science.

Yamin, J., Abu-Zaid, M., Badran, O. 2006. Comparative Performance of Spark Ignition Engine Using Blends of Various Methanol Percentages with Low Octane Number Gasoline. International Journal of Environment and Pollution. Vol. 23(3): 336-334.

2013 USDA- Foreign Agricultural Service, Global Agricultural Information Network (GAIN) Report

Acknowledgement

The MMSU Bioethanol Team would like to acknowledge the full support of Mariano Marcos State University and the financial support of the Department of Energy, PhilRice, and DOST-I/ICIERRD.

Short Description of the Technology

The paper present the production technologies for hydrous ethanol at the village scale. The improved and optimized fermentation protocols using sweet sorghum involved 30 mins yeast activation at elevated temperature of 30-32°C, reconstitution of residual sugar (14-15°Brix) to 30°Brix by adding sweet sorghum syrup rather than concentrating it to increase sugar concentration, and fermentation period of 72hrs. These condition would give fermentation efficiency of 85%. For naturally fermenting nipa sap, high ethanol yield is best obtained under facultative anaerobic protocol.

Improved reflux distillation system afforded 93-98% recovery of 95% azeotrope ethanol. Unlike the previous designs, the reflux kettle and reflux tower are equipped with digital temperature gauges and pressure valves for safety operation. The condenser is cooled with a circulating water from the cooling tower, hence zero water wastage. The furnace was improved at much reduced fuel wood input due to shortened distillation time. Ethanol output from the condenser is totally liquefied and cold. The most significant improvement of the optimized distillation facility is its high efficiency in recovering 95% pure ethanol from the beer skipping much time and energy for second distillation. The facility can process bioethanol from different feedstock including palm juice, like the nipa sap.