# BIOHYDROGEN AS AN ALTERNATIVE ENERGY SOURCE FOR CUBA

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The deteriorated energy infrastructure of Cuba provides an opportunity to explore completely new forms of energy production. This report evaluates the potential of biohydrogen, the biological production of hydrogen fuel. Biohydrogen is chosen because it is a sustainable, renewable, and a clean energy source characterized by relatively low capital costs. We consider Cuba as an ideal location for a biohydrogen economy because of the need to reconstruct the country's energy sector and its ability to produce the substrate-sugarcane bagasse-needed for the biological process. We specifically explore historical trends of sugarcane production in Cuba, the potential of sugarcane bagasse to serve as the primary substrate for the growth of the hydrogen-producing bacteria, and the amount of energy that can be potentially produced from the process. Biohydrogen processes evaluated include dark fermentation and the most recent technology, microbial electrolysis cells (MECs). The chosen pilot design is based upon a coupled system that combines dark fermentation and MECs. Based upon literature values, the chosen process was sized for the production of a 1 kW fuel cell, which is enough to power a modest home. Recommendations and limitations of the technology are described.

#### WHY BIOHYDROGEN?

One of the biggest challenges facing society today is climate change. The constant discharge of greenhouse gases, such as carbon dioxide, methane, and nitrous oxide, into the atmosphere has resulted in temperature increases of the Earth's atmosphere (Garrison, 2005). The carbon dioxide (CO<sub>2</sub>) concentrations in our atmosphere have dramatically increased since the Industrial Revolution. About 80% of greenhouse gas emissions consist of CO<sub>2</sub> due to the burning of fossil fuels. As of 2005, there was an estimated concentration of  $CO_2$  in the atmosphere of 380 ppm (parts per million), which is the highest concentration measured in a 600,000-year record (Gore, 2006). Fossil fuels are burned primarily to generate electricity at power plants and various forms of transportation. In addition to the environmental implications, fossil fuel reservoirs are limited and their costs are high (Kalia and Purohit, 2008). Newer and cleaner alternative energy sources are an inevitable development in order for societies to strengthen their economic security as well as aiding in the restoration of global climate.

Many emerging alternative technologies are geared towards providing cleaner energy, and are being implemented in many places around the world. Howev-

<sup>1.</sup> Editor's Note: This paper was submitted to the ASCE 2013 Student Prize Competition for Undergraduate Students.

<sup>2.</sup> The authors acknowledge the assistance received from Dr. Helena Solo-Gabriele our faculty advisor for this project. We also acknowledge the information received from Dr. Nejat Veziroglu about the benefits of hydrogen energy and from Dr. Manuel Cereijo about energy usage and the characteristics of sugar mills in Cuba. We also appreciate the comments received from Drs. Joseph Scarpaci, Enrique Pumar, and Jorge Pérez-López. The technical appendices and calculations are available at https://umshare.miami.edu/web/ wda/engineeringfiles/CAE/ASCE\_Biohydrogen.pdf.

er, their costs are generally high, and most developing countries are not able to invest in the infrastructure needed to harness them. Another drawback of some forms of alternative energy is the fluctuating production. Therefore, the conversion to a form of storable fuel in order to meet energy demands is required, increasing the cost of their use even more (Kalia and Purohit, 2008).

Some of these alternative energies include: thermonuclear energy, solar energy, wind energy, hydroelectric energy, radiant energy, tidal energy, and bio-fuels. Unlike most alternative energies, biofuels can be stored and later transported for use. Biofuels are fuels produced by living organisms that tend to be cheaper than other renewable alternative energies as they can be generated from biological wastes and water (Kalia and Purohit, 2008).

Second-generation biofuels are still under development and include: algae fuel, cellulosic ethanol, biomethanol, and biohydrogen. Biohydrogen involves the production of hydrogen gas typically by organisms such as algae, archaea, and bacteria. Hydrogen has a very high energy content of 120 MJ/kg versus 44 MJ/kg of gasoline (Lalaurette et al, 2009), that is, 2.75 times greater than hydrocarbon fuel, which means it has a very high economic value per unit weight (Pattra et al, 2008). Hydrogen is easier and safer to handle than other fuels used to produce energy or transportation, it is easily collected, stored, and transported, and it produces water upon combustion (Kalia and Purohit, 2008). Hydrogen fuel when burned does not radiate heat and is not poisonous (Veziroglu, personal communication).

There are multiple methods to biologically produce hydrogen, which include the use of fermentative hydrogen-producing bacteria, microbial electrolysis cells, biophotolysis, among others. These methods, aside from being more affordable than other energy producing techniques, are non-polluting and can be used in developing nations by utilizing already existing bio-wastes.

# Why Cuba?

The Republic of Cuba encompasses over one hundred thousand square miles of land of which over 50% is arable. It is located approximately 90 miles away from the United States and lies at the entrance of the Yucatan Peninsula, making this country of great geographical importance from a trade perspective.

Cuba's major commodities include nickel, coffee, tobacco, fish, medical products, and sugar. In the 1920s Cuba was one of the world's leading sugarcane producers. However, in 1959 the government began to nationalize the agricultural sector and foreign trade activities. In early 1960, agreements were made with the Soviet Union to exchange sugar for Soviet oil. The goal of the sugar industry in Cuba was to increase the amount of sugar production, rather than seeking to increase its efficiency (Salazar-Carrillo, 2002). This led to the mechanization of the Cuban sugar industry, ultimately increasing Cuba's dependency on foreign oil. The Soviet Union disintegrated in the 1990s, and stopped providing oil imports in exchange for sugar. This coupled with competition in the global sugar market, led to the creation of a National Energy Sources Development Program to promote the use of Cuba's energy resources and minimize energy imports. However, high sulfur concentrations contained in Cuba's domestic oil and lack of maintenance caused infrastructure damage and frequent blackouts. Hurricanes further damaged the power distribution system, resulting in an energy crisis in 2005. Currently, Cuba's energy sector depends heavily on oil imports, primarily under an agreement regarding trade of crude oil and derivatives from Venezuela (Suárez et al., 2012).

These changes further deteriorated the Cuban economy, and have negatively impacted sugarcane production (Peters, 2003). Figure 1 illustrates the locations of Cuba's sugar mills. Considering that the sugarcane mills in Cuba are well distributed across the island, transportation costs are minimal and appealing if sugarcane bagasse were to be utilized as a fuel for energy generation.

As mentioned, the Cuban sugar agro-industry began to falter in the 1990s. Growth slowed again in 1998 and sugar production became uneconomical. Initial plans of dismantling some of the sugar mills for other agricultural crops were suggested. Ultimately, a restructuring plan was proposed by the Cuban govern-



# Figure 1. GIS Map of Known Locations of Sugar Mills in Cuba (Adapted from SSatelliteviews.net)

ment in 2002 to permanently shut down about half of the existing 156 sugar mills due to depressed world-market sugar prices. The restructuring plan consisted of deactivating 71 of the 156 existing sugarcane mills; out of the 71 sugarcane mills deactivated, 5 mills would be converted into museums, 5 mills would remain idle, and the rest would be dismantled (Alvarez, 2006). The exact number of existing sugarcane mills is unknown at this time (Manuel Cereijo, personal communication). The environmental protection and economic growth of Cuba will require research in the adaptation and the sustainable use of Cuba's natural resources. Biohydrogen technology may be a promising alternative solution to Cuba's energy deficiency and the answer to end dependency on fossil fuels.

#### Sugarcane Bagasse

Wastes such as lignocellulosic material, and industrial and household wastewater are sustainable resources that can be utilized to generate energy. A method that generates energy from such resources aids in the minimization of costs and waste due to their low commercial value. Lignocellulosic biomass is the most readily available and affordable resource in nature. In Cuba, lignocellulose is abundant and can be obtained through the processing of sugarcane, as waste arising from this process. This waste is referred to as sugarcane bagasse, which is mainly composed of lignocellulose. The combustion of the bagasse is the traditional method of obtaining energy to meet the power demand of the sugarcane mills. Bagasse is also used in various processes that fabricate pulp, paper, fiberboards, and activated charcoal. It is also used in the hydrolysis industry for furfural and ethanol production.

### **Power Needs**

In Cuba, there is an evident need for a reliable, economical, and sustainable system to produce energy. The power plants in Cuba are old and poorly maintained, resulting in an inefficient and unpredictable power capacity. Cuba's energy grid is in need of significant upgrades with cost estimates in the billions of dollars. Modernization of Cuba's power infrastructure should consider both the development of a smart grid and smart generation (Cereijo & Solo-Gabriele, 2011). Future power generation will rely heavily upon the decision to utilize fuel oil versus natural gas and to supplement power production with alternative technologies that rely on wind, biomass, solar, nuclear power (Cereijo, 2010), and possibly biohydrogen. Thermoelectric plants constitute the majority (61%) of the installed power capacity in Cuba, as illustrated in Figure 2. It is followed by small generators, also referred to as "batteries," with 31%, while 8% originates from the growing natural gas industry. Lastly, 1% of the installed capacity corresponds to biomass and wind farming. However, 35% of electricity produced is lost due to Cuba's deteriorating infrastructure (Cereijo, 2010).

# Figure 2. Installed Power Capacity in Cuba (from Cereijo, 2010)



The production of hydrogen gas can be theoretically implemented on a large scale by using the natural resources already there. As mentioned, the waste from sugarcane production, sugarcane bagasse, can be used by bacteria to produce hydrogen via fermentation and microbial electrolysis cells. Thus, biohydrogen appears to be a promising energy alternative for Cuba, given the country's natural resources and the possibility of an independent source of fuel energy.

# **BIOHYDROGEN PROCESSES**

Hydrogen gas  $(H_2)$  can be generated through the action of microbes through several different processes. These include fermentation (both light and dark), microbial electrolysis cells (MEC), and through various combinations of these processes including the use of microbial fuel cells to generate the electricity needed for MECs.

### **Microbial Fermentation**

Fermentation is one of the less expensive techniques for the biological production of hydrogen gas (Kalia and Purohit, 2008). The dark-fermentation process is preferred because it does not rely on the availability of light and can occur continuously in a reactor (Manikkandan et al, 2009). The fermentation process uses anaerobic digestion and complex biochemical reactions for the microbial growth to produce energy. Growth and the subsequent production of hydrogen is dependent upon many factors including pH, temperature, time of reaction, and most importantly, the substrate used by the microorganisms. There are many different substrates that can be used in the fermentation process. The classic substrate is glucose, which is found in sugarcane bagasse, corn pulp, and raw starch of corn, among many others. Figure 3 shows that glucose is a very effective substrate for biohydrogen generation.

# Figure 3. Hydrogen Production from Fermentation Processes that Utilize Different Substrates (from Logan et al. 2002)



The anaerobic metabolism of glucose is a process known as glycolysis. This process yields pyruvate, which is broken down into compounds and becomes an energy source for the organisms. These energy source compounds are adenosine triphosphate (ATP) and reduced nicotinamide adenine dinucleotide (NADH) (Kalia and Purohit, 2008).

Because the substrate is so important to maximize the yield of hydrogen, it is essential to find a bio-waste

that has high potential. Sugarcane bagasse is the waste left after the sugarcane extraction process and accounts for approximately 25% of the sugarcane crop yield. The sugarcane bio-waste is made up of three different fractions: cellulose, hemicellulose, and lignin (Pattra et al, 2008). For the organisms to use bagasse as a substrate during anaerobic fermentation, it must first be hydrolyzed, which is usually done with small amounts of sulfuric acid (Manikkandan et al, 2009). It is the hemicellulose in the bagasse that reacts with the acid and yields glucose and xylose. The other two components, cellulose and lignin, form a solid waste. The amount of substrate produced from sugarcane waste can then be calculated as approximately 30-35% of the bagasse, which is the portion composed of hemicellulose (Pattra et al, 2008).

To convert the raw bagasse to the substrate that the bacteria will ferment, the bagasse must first be treated with adequate amounts of sulfuric acid. Too much acid may inhibit bacterial growth and shorten the life use of equipment by corrosion. Manikkandan et al, 2008 found that small amounts of the acid with extended hydrolysis times yield higher glucose concentrations. The production of hydrogen relies heavily on the initial pH of the production. As noted in Table 1, the optimum initial pH of different bacteria strains varies. The pH also influences the rate yielding. Really low pH may increase formation of weak acids, which destabilizes the cell's ability to maintain internal pH, damages the cell membrane, proteins and DNA, slowing down or completely inhibiting cell production. Numerous research indicates that for fermentation, the pH at which this may occur is 5.0 and below (Pattra et al, 2008).

# Table 1.Comparison of Dark FermentationBacteria (from Manikkandan etal., 2009 and Pattra et al., 2008)

-					H <sub>2</sub> Yield (mol
					H <sub>2</sub> / mol
Bacteria	Substrate	pН	Temperature	Time	substrate)
Bacillus sp.	Glucose	7.0	32°C	48 hrs	0.23
Clostridium					
butyricum	Glucose	5.5	37°C	40 hrs	1.73

through the MFC process, a continuous supply of

The production of hydrogen increases as the initial bagasse extract concentration also increases. However, continuous increase in concentration of bagasse extract affects the organism's growth rate, dropping drastically the production of hydrogen (Manikkandan et al, 2009). Temperature is yet another factor that must be monitored in microbial hydrogen production. The optimum temperature that several authors have reported is  $32^{\circ}$ C. Manikkandan et al, 2009 found that for *Bacillus sp.*, the production rate at 40°C dropped significantly due to protein deactivation. However, the use of acclimated pure or mixed cultures has had high conversion efficiencies at  $37^{\circ}$ C (Logan et al, 2002).

The time for reaction as well as the other factors affecting production depends on the specific bacteria. For example, while *Bacillus sp.* has a maximum hydrogen production of 0.23 mol of H<sub>2</sub> per mol of substrate under optimized conditions at 48hr (Manikkandan et al, 2009), *C. butyricum* achieved maximum yield of 1.73 mol of H<sub>2</sub> per mol of substrate, under optimized condition, in just 40 hours.

#### **Bioelectrochemical Systems**

The microbial electrolysis cell (MEC) is one of the latest emerging techonolgies in biohydrogen production. Its discovery originates from modified microbial fuel cell (MFC) designs. Both devices are referred to as bioelectrochemical systems (BES), where microorganisms serve as catalysts for the electrochemical reactions that occur in the bioanode of the cell. As opposed to MFCs, which generate current, MECs require electricity for the production of hydrogen. Figure 4 illustrates the two processes. MFCs consist of the biocatalyzed electron transfer from the anode to the cathode of the cell. Bacteria in the anode compartment oxidize organic matter, releasing carbon dioxide and protons in the solution, and electrons to the anode. The protons are transferred to the cathode chamber through a cation specific membrane, while the electrons are transferred to the cathode chamber through an external electric circuit. Under aerobic conditions, the protons and the electrons are consumed in the cathode chamber by combining with oxygen to form water. In order to generate a current substrate must be supplied at the anode.

Figure 4. Illustration of the Microbial Fuel Cell (MFC) [Panel (a)] and the Microbial Electrolysis Cell (MEC) [Panel (b)]



The MEC process is nonspontaneous and it requires an external source of energy to drive the electrochemical reactions. Under anaerobic conditions, applying a small amount of voltage (> 0.2 V) between the anode and the cathode drives the production of hydrogen. This process is now known as electrohydrogenesis or microbial electrolysis. The MEC is not entirely sustainable because the cell requires an external energy source in the form of electricity. However, a MFC can provide the power required by a MEC, resulting in a MEC-MFC coupled system (Sun et al., 2009; Hatzell et al., 2013).

# **BES Reactor Design**

Early experiments utilized a traditional and inexpensive design to demonstrate the concept of BESs. Characterized by its H-shape, the design consists of two bottles connected by a tube and a cation/proton exchange membrane (e.g., Nafion or Ultrex) or a salt bridge that assists the movement of protons from the anode to the cathode of the cell, while isolating the substrate (Figure 5). In the case of a MEC, a gas collection and release system accompanies the cathode. Furthermore, BES efficiency was successfully improved by increasing the size of the membrane and the surface area of the anode with the addition of graphite granules. (Logan et al, 2006, Logan et al, 2008).

As previously mentioned, the presence of oxygen in the cathode creates the necessary potential to create a





spontaneous current. Therefore, the cathode of a MFC can be placed in direct contact with air, regardless of the presence of a membrane. A membrane is employed to prevent water from leaking to the cathode and oxygen from reaching the anode, while oxygen is consumed by bacteria, resulting in a lower Coulombic efficiency and lower hydrostatic pressures. Further modifications have led to continuous flow designs including the upflow fixed-bed biofilm reactor, in which fluid flows through porous anodes toward a membrane that separates the two opposing chambers (Logan et al, 2006). The MEC reactor volume can be reduced by integrating the membrane with the cathode and placing a platinum catalyst layer that faces the gas collection system, eliminating the surrounding liquid in the cathode chamber. In MECs, however, the membrane is not essential due to its anerobic conditions. Thus, single-chambered MECs that lack a membrane simplify reactor design and reduce costs.

# **Electrode Material**

**Bioanode.** Several studies have evaluated BES performance by operating the bioanode with mixed or pure cultures of microbes. Laboratory-scale BES open systems are commonly enriched with pure cultures, while larger-scale experimental designs utilize mixed cultures. The microbial diversity of the cultures may vary as they are enriched using inocula from natural resources such as soil, anaerobic sediment sludge, and wastewater treatment sludge (Pham et al, 2009).

Anodic material that efficiently interacts with the microorganisms and the substrate should be biocompatible, non-corrosive, conductive, and cost-effective. Anodes commonly consist of carbon in the form of compact graphite plates, rods, granules, graphite brush, fibrous materials, or glassy carbon due to their defined surface area and simple use.

**Cathode.** Electrons are consumed in the cathode chamber, where oxygen is reduced to water in a MFC, while hydrogen gas evolves in a MEC. The catalytic base material of the cathode significantly influences the efficiency of the cell and, as the anode, must be non-corrosive, conductive, and possess an efficient surface area. It may be graphite, titanium or other conductive metal. Hydrogen evolution on plain carbon is slow and a conductive metal, such as platinum, is usually the preferred catalyst. Due to the high cost of platinum, researchers suggest noble-metal free catalysts that use pyrolyzed iron(II) phthalocyanine or CoTMPP (Logan et al, 2006) or stainless steel, MoS2, and nickel foam (Kundu et al, 2012).

# DESIGN

As previously mentioned, hydrogen gas is generated in the presence of bacteria, whose catalysts aid in the electrochemical reaction between protons and electrons during fermentation. However, bacteria use additional metabolic paths that lead to the production of various end-products such as acetate, butyrate, and ethanol that reduce hydrogen yield. Further breakdown of this organic matter is nonspontaneous and requires an external source of energy. An alternative approach considers the combination of two or more biological processes to attain greater hydrogen production rates.

In this section, a coupled system that combines dark fermentation and a microbial electrolysis cell to produce biohydrogen from sugarcane waste is proposed. Methods (i.e., calculations for reactor volume) and data (i.e., hydrogen production rates) were obtained from the literature to design the system. The substrate, sugarcane bagasse, initially undergoes hydrolysis, followed by fermentation and electrohydrogenesis. Lastly, the necessary hydrogen gas produced by both processes is collected in a storage tank and transferred to 1-kW fuel cell for electricity production. To further extract hydrogen gas from organic matter that cannot be broken down during fermentation, various studies have examined the performance of this two stage process, in which the fermentation effluent is fed into a MEC.

In a study performed by Lu et al. (2009), a membraneless, single-chamber MEC was fed with the effluent from an ethanol-type dark-fermentation reactor. The continuous stirred-tank reactor was fed with molasses wastewater and produced hydrogen gas at a maximum rate of 0.70m3 H<sub>2</sub>/m3/d. The effluent contained ethanol, acetic acid, propionic acid, butyric acid, and valeric acid. To prepare the MECs, MFCs were inoculated with domestic wastewater and the cathodes were aerated. The new MECs were fed with buffered effluent from the fermentation process after changing the polarity of the MFCs. The application of 0.6 V resulted in a maximum hydrogen production rate of 1.41±0.08m3 H<sub>2</sub>/m3/d. The absence of a membrane allowed for a higher current density, which resulted in higher hydrogen production rate.

A separate study conducted by Lalaurette et al. (2009) examines the conversion of lignocellulose and cellobiose into hydrogen gas through a two-stage process, in which electrohydrogenesis in a MEC is followed by fermentation. A pure culture of *Clostrid-ium thermocellum* was utilized for the fermentation process, and the MEC was inoculated with wastewater and fed with the fermentation effluent. During the fermentation, pre-treated lignocellulosic biomass was converted into hydrogen, carbon dioxide, acetic, formic, succinic, and lactic acids, and ethanol. The organic end-products constitute the effluent that was decomposed in the MEC to generate biohydrogen. Furthermore, the two-stage process attained an overall hydrogen production yield of 9.95 mol H<sub>2</sub>/mol glucose from cellobiose.

Volumes of the reactors were calculated using the method shown in technical appendix Ca. According to Pattra et al., 25% of sugar production that results in waste consists of 30-35% of hemicellulose, and the rest of cellulose and lignin. Hemicellulose is obtained from the hydrolysis of sugarcane bagasse and can be fermented, while lignin and cellulose remain as solids. A settling tank following hydrolysis separates the solids, and the solution containing hemicellulose is fed into a fermentation batch reactor, as done by Pattra et al. (2008). The effluent from the fermentation reactor and precipitate from the settling tank are fed into the MEC. A hydrogen production rate of 1611 mL L-1 hr-1 obtained by Pattra et al. during the fermentation of sugarcane bagasse, and that obtained by Lalaurette et al. (2009) during the electrohydrogenesis of lignocellulose were used to determine the total hydrogen production to power a 1 kW fuel cell.<sup>3</sup>

A total hydrogen production rate of 4.4 mmol L-1 hr-1 resulted in fermentation and MEC reactor volumes of approximately 3,450 L and 8,700 L respectively. In addition, a volume of approximately 860 L was calculated for the hydrolysis process. The systems that are commonly implemented for hydrolysis and fermentation are batch or continuous stirred tank reactors. A heating unit for the entire integrated system

is necessary to maintain the desired temperature for each of the processes. Lastly, a voltage range of 0.2-0.6 V is required to power the MEC. As found in the literature, this may be supplied by a MFC, resulting in a fully sustainable integrated system for biohydrogen production (Wang et al., 2011). Further research into this area is necessary to fully assess the utilization of a MFC that provides the required 0.6 V of a MEC. Nevertheless, integrating the two bioelectrochemical technologies and fermentation in a two stage process is an innovative idea of creating a system that sustains the conversion of biomass into hydrogen without an external source of energy. Figures 6 and 7 illustrate the coupled fermentation-MEC system that utilizes sugarcane bagasse as the substrate. Cost estimates for the system suggest a total cost of \$408,000.4

### CONCLUSION AND RECOMMENDATIONS

In order to generate 1 kW of energy, which is the amount needed for a modest home, we estimate that 25.2 acres of sugarcane fields would be needed to provide the substrate for the process. Figure 8 displays the sugarcane production rate in Cuba from 1984 to 2010. In 1989, a peak of approximately 81.8 million metric tons of sugarcane harvested was achieved (Anuario Estadístico de Cuba 2011, 2012). Assuming that only the bagasse waste is utilized for biohydrogen production, this area represents about 160 MW of electricity given the technology available today.<sup>5</sup> This is enough energy to provide power to almost 160,000 modest sized homes. Assuming that 4 people live per home, this represents the provision of power for nearly 640,000 residents. If the entire sugarcane crop, as opposed to only the bagasse waste, were utilized for the production of energy, Cuba's sugarcane agriculture would be capable of theoretically providing 640 MW of electricity which could serve part of the country's energy needs. In addition, Figure 9 displays the potential power generation

<sup>3.</sup> https://umshare.miami.edu/web/wda/engineeringfiles/CAE/ASCE\_Biohydrogen.pdf. See Appendix C, "Design Computations for Sizing Reactor Volumes."

<sup>4.</sup> https://umshare.miami.edu/web/wda/engineeringfiles/CAE/ASCE\_Biohydrogen.pdf. See Appendix D, "Cost Analysis."

<sup>5.</sup> https://umshare.miami.edu/web/wda/engineeringfiles/CAE/ASCE\_Biohydrogen.pdf. See Appendix E, "Cuba Potential Power Generation in 1989."





Figure 7. Fermentation-MEC System Design for the Trajectory of the Bagasse and its Usage to Produce Hydrogen



based on recent sugarcane harvest data. Recent speculations on Cuban sugar harvest show rising production in the last year (Fox News Latino, 2012). With improvements in technology, sugarcane production, profitability and enterprise sector there is a potential for sugarcane and the bagasse waste to provide a greater amount of hydrogen energy per acre of harvested land. Figure 8. Sugarcane Production in Cuba from 1984 to 2010 in Million Metric Tons (Adapted from *Anuario Estadístico de Cuba* 2011, 2012)



Our preliminary design shows encouraging results and demonstrates the possibility of producing biohydrogen from readily available resources, such as sugarcane bagasse or other lignocellulosic biomass. It is important to note that our design is based on experimental results obtained through laboratory scale methods. Therefore, assumptions were made in order

# Figure 9. Power Potential Based on Sugarcane Harvest per year from 1984 to 2010 in Cuba in MW



to scale up the processes. Further research into bioelectrochemical processes is necessary to enhance the process efficiency and performance. A full-scale prototype is recommended to further analyze hydrogen production. The utilization of this technology can potentially provide a promising alternative for power generation in Cuba, especially in areas where sugarcane is harvested.

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