Hydrogen from Microalgae and the Collection and Sensing Systems

Interim Design Report

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Born and raised in Jacksonville, Florida, Ariel Johnson is currently a student enrolled at the Florida State University majoring in Mechanical Engineering. She has participated in the Air Force ROTC program for 2 years since her collegiate experience started in the summer of 2010, and would like to serve her country as an Officer in the Air Force upon graduation.

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Born In Patagonia, Argentina, Jon is currently a mechanical engineering student at Florida State University. During his studies at FSU, Jon has worked at FCAAP under the supervision of Dr. Farrukh Alvi in high velocity fluid mechanics. After graduating he plans on attending graduate school at UCF and later hopes to work in the film industry or in renewable energy applications.

BRAZIL TEAM

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Born and raised as a military child, Nicole has had the opportunity to grow up around the world, including many states in the USA, Italy, Argentina, and Bolivia. She is currently studying mechanical engineering at FSU and has held internship positions with Rolls-Royce and Pratt & Whitney. Her work within and outside of school has grown her interest to pursue a career in the aerospace industry.

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Ben is a senior graduating from Florida State University in May, 2015 with a Bachelor of Science in Mechanical Engineering. He is currently working in Curitiba, Brazil at Universidade Federal do Paraná studying microalgae growth and calibrating a hydrogen sensor with a team of American and Brazilian students. His effective communication skills have helped foster the continuing success of this international team.

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Richard is in his 4th year at Florida state university and is pursuing a BS in Chemical Engineering with a business minor. He is interested in a career in the oil and energy industry and work towards finding alternative forms of sustainable energy.

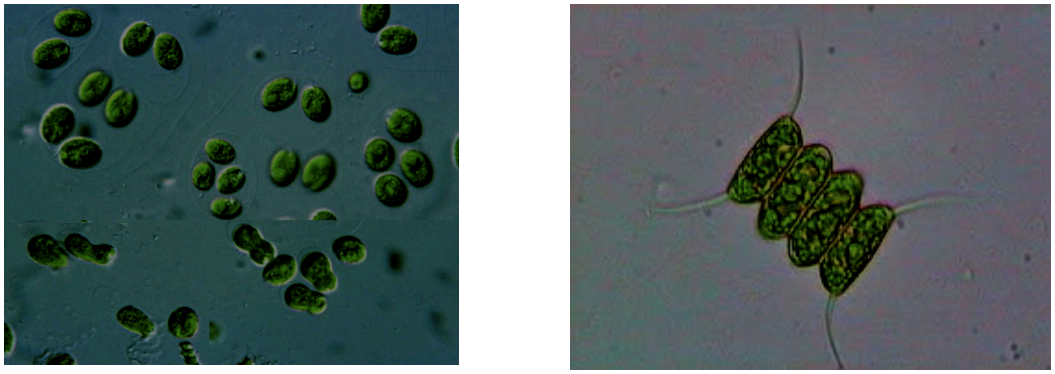
Abstract* -- Although it may not be readily apparent, energy directly correlates with the quality of life and technological resources that are available to people. As societies grow and become more advanced, the consumption and need for more energy increases. The augmented demand can put a strain on available resources which is why there has been a heightened interest in alternative energy. This project will focus on hydrogen as an alternative energy source. A photobioreactor has been developed which uses the hydrogen gases produced by microalgae *Chlamydomonas reinhardtii* and *Scendesmus sp* to create energy. This project seeks to improve microalgae cultivation and develop a sensor to accurately measure the amount of hydrogen production. Under optimal conditions, hydrogen output is expected to be 10.2$\frac{mL}{h}$ for *Chlamydomonas reinhardtii* and 0.167 $\frac{mL}{h}$ for *Scendesmus sp.

I. INTRODUCTION

Hydrogen gas has become an ideal fuel source for the future since it burns clean and generates a large amount of energy per unit mass allowing it to be more fuel-efficient than other resources [1]. Using hydrogen in renewable energy processes has become of greater interest due to the depletion of natural oil reserves. However, because of low concentrations at its pure form, hydrogen is not cost efficient for everyday use, making the study of biohydrogen one of great interest [2]. This calls for the exploration of hydrogen generation as a waste product of anaerobic respiration of green and blue algae from a photo bioreactor. When a controlled environment enables and regulates the proper anaerobic conditions necessary for the cultivation of algae, a photobioreactor is constructed to allow larger amounts of bio hydrogen to be produced and utilized as clean energy [3]. This occurs through biophytolysis of water by algae. The presence of light irradiation catalyzes the event and water is broken down into its hydrogen and oxygen components [4]. The phenomenon in which hydrogen is created as a waste product during the photosynthesis of algae must be promoted in a way that overcomes various issues [5]. These issues include creating a system that enables steady and continuous microalgae growth that is cost effective. The evolution of hydrogen results in an amount of fuel that is useable in commercial applications. The scope of this project will be directed toward the design and development of microalgae and measuring and collecting the hydrogen produced.

In today's world the need for renewable/sustainable energy has never been greater. Coal, petroleum, and other types of non-renewable sources provide much of the energy used today. Within the next century, these energy resources are projected to be fully depleted. Hydrogen is at the top of the list of biofuels that can solve the energy crisis that future generations face. Hydrogen in the simplest element known to man and it is usually combined with other elements. For example, hydrogen combines with oxygen to form H_2O, the most abundant resource on our planet [1]. However, it has proven difficult and expensive to split hydrogen from water to use as an energy source [2]. The most common form of this element is found as hydrocarbons, a product of organic compounds, which makes up gasoline, methanol, and propane. Hydrogen can be extracted from hydrocarbons through the application of heat, a process known as reforming [1]. The downside of reforming is the byproduct CO2, which contributes to the greenhouse effect.

One alternative for hydrogen production comes from algae. Using sunlight as their energy source, and under the right conditions, algae can give off hydrogen. The research that is currently being done is aimed at two



(a) **(b)**

Fig 1: (a) *Scenedesmus sp.* (b) *Chlamydomonas reinhardtii*

types of algae: Scenedesmus sp. and Chlamydomonas reinhardti, figure 1a and 1b, respectively. These types of algae are favored due to their high degree of adaptability and fast reproductive cycle [3]. Our sponsor has given us the primary tasks of designing and developing an H_2 producing photobioreactor, and designing and developing an electronic H_2 mass measuring sensor to test such systems.

In order to produce H_2 from algae, the algae must be cultivated in a controlled manner. There are two ways to cultivate algae: open ponds and photobioreactors. Photobioreactors (PBRs) are closed systems that provide a controlled environment where algae productivity is high. PBRs are used to better control CO_2 supply, water supply, temperature, etc. [4]. Figure 2 shows a basic schematic of a PBR. The main components of such a system include a light source, hot plate, thermocouple, container, and a gas collection apparatus. Previous senior design teams at Florida State University have built working photobioreactors. One such team was team 7 from 2013 who was successful in designing and fabricating a bioreactor, which can be seen in figure 3. Their bioreactor has sensors that can monitor algae concentration, mass flow rate, and CO_2 concentrations. The bioreactor is installed in the AME building at the FAMU-FSU engineering school.

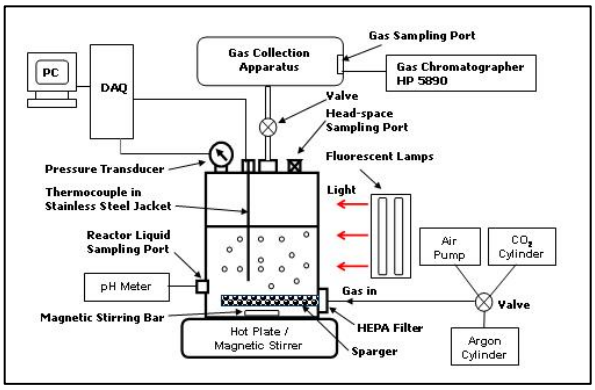


Fig 2: Schematic of a Photobioreactor.

A. Need Statement

Florida State University and the Federal University of Parana have joined together to sponsor this project. There is need for a scalable and sustainable process for producing hydrogen from microalgae cultures such as Scenedesmus sp. and *Chlamydomonas reinhardtii* to demonstrate the feasibility of photobioreactors in the field of alternative energy. Additionally, an automated sensing system will be needed to monitor the hydrogen content of the resulting PBR system.

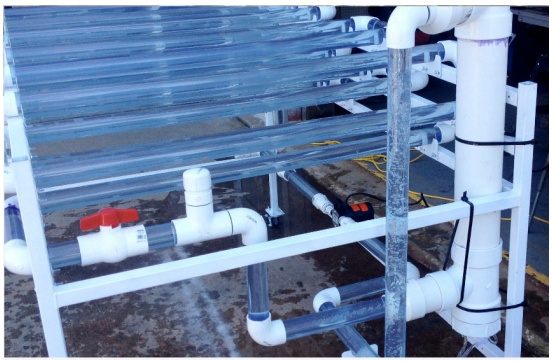


Fig 3: Team 7's 2013 photobioreactor

B. Goal Statement

The goal of this project is to further the development of alternative energy with the use of a sustainable process for producing hydrogen from microalgae. To consider this project as successfully completed, the project sponsor provided several objectives that need to be met.

C. Objectives and Sponsor Requirement

The sponsors of this project include Florida State University and the Federal University of Parana. They have asked that we pursue and complete the following general project and prototype objectives:

General Project Objectives

- Design and construct operational H_2 producing units
- Design and construct an electronic H_2 mass measuring sensor
- Provide enough experimental data to test the operation of the H_2 producing designed units
- Provide mechanical drawings of the entire system and sensor for future product scale up
- Write an invention disclosure (FSU team) to be submitted to the USPTO by the OTT/FSU, and a patent request (Brazilian team) to be submitted to the Brazilian INPI, for the H_2 producing photo bioreactor system developed

Prototype Objectives

- It should be fully automated
- It should be low-cost
- It should be readily scalable

D. Constraints

There are many engineering issues such as appropriate bioreactor designs and scaling-up the system, preventing interspecies hydrogen transfer to non-sterile conditions, and the purification and separation of hydrogen. The photobioreactor should be designed in such a way that it is easily scalable. The workspace in the lab is small which means the size of our bioreactor will be smaller. Because of space restrictions, the size of the bioreactor was changed from 8' x 3' to 4' by 3'. However, if this type of system is to potentially be used as a major source of energy in the future, a much larger bioreactor is needed. The bioreactor also cannot be used until a gallon of algae is grown. Until then, the algae will initially be grown in small glass bottles or beakers.

Our team is working with a budget of roughly $1000. This creates issues when it comes to growing and maintaining healthy algae. The food for the algae is very expensive to buy premade so it is important for the team to learn how to make the food. The biggest constraint for this project deals with maintaining a large amount of healthy algae and the time is takes to produce that amount. It can take weeks to grow an adequate amount of algae and without a large amount, hydrogen production won't be maximized. Many of the students working on this project have little background in the growth processes of microalgae and microorganisms in general. This insufficient knowledge could lead to a lack of understanding on how to integrate hydrogen production with other processes. The processing of biomass feed stock is also very expensive. If this it to become a widespread energy source in the future, the cost of production must be reduced.

The hydrogen mass sensor must have three different colored LED lights that correspond with different percentage levels (5%, 10%, 20%) of hydrogen mass. The lights will light up according to the mass percentage detected. It will also make a sound once the hydrogen mass percentage level is above 5%.

II. DESIGN AND ANALYSIS

There are four main components that are essential to successful production and storage of hydrogen: hydrogen generator, hydrogen refiner, hydrogen compressor, and a pressure vessel[10]. In this project, an airlift bioreactor was designed to cultivate algae, which would generate hydrogen. The hydrogen gas sensor will be attached to the gas outlet to measure the concentration of hydrogen. Once the hydrogen has reached the desired concentration level, gases will enter the hydrogen refiner. Along with hydrogen, there will be many other gases present in the bioreactor. The gas purifier is used to refine the hydrogen and separate it from unwanted gases and contaminants resulting in a pure form of hydrogen. After refining, the purified hydrogen will flow through a mechanical compressor so that it may be safely stored in a compressed tank.

A. Design

Due to time and budget constraints, it was necessary to use a previously constructed photobioreactor. The decision was made to use the prototype built by the 2014 senior design team. This design was chosen because of its simplicity and the fact that it is an airlift bioreactor, which has the advantages of good mixing, effective mass transfer of CO_2, high S/V ratio, and good removal of O_2. The final 2014 design can be seen in figure 4(a). After analyzing the 2014 senior design team's prototype, several modifications would have to be made to optimize the system for hydrogen production. The current proposed final design can be seen in figure 4(b). The first change made to the design was the increase in size, and the change in the horizontal angle of the upper horizontal tube, known as the gas separator. This component is critical for gas exchange i.e. where hydrogen bubbles separating from the liquid to air. Gas exchange can only occur if there is headspace in the gas separator. This design criteria was omitted from the previous year's prototype because their purpose was to extract biomass not hydrogen. The horizontal angle of the gas separator will also be modified. An angle of three degrees will be implemented to prevent gas buildup and allow the hydrogen to move towards the exhaust port. This angle can be altered if complications arise.

Another significant change to the previous design is a reduction in the diameter of the down-comer tube, which is the vertical tube on the left side. The reduction in diameter improves gas holdup, which is the volume ratio of gas to liquid within the reactor. In addition, gas holdup has a heavy influence on CO_2 mass transfer, gas bubble velocity, and H_2 production. Pressure differences occur between the down-comer and riser if the diameters of each are the same. By reducing the diameter of the down-comer the pressure difference will decrease, gas holdup and superficial gas velocity will increase, which are important properties that impact hydrogen output. It can also be seen in figure 4 that the height of the bioreactor was modified. The previous team's design was 8 feet tall while the current proposed design will be roughly 4 feet tall. The reduction in height was necessary to artificially light the

reactor and to reduce the pressure supplied for the air pump. As the reactor height increases so does the fluid pressure at the diffuser. The pumping pressure necessary to overcome the pressure induced by the column height will also increase and produce a greater shear stress on the algae, which can exceed the max shear stress of the algae

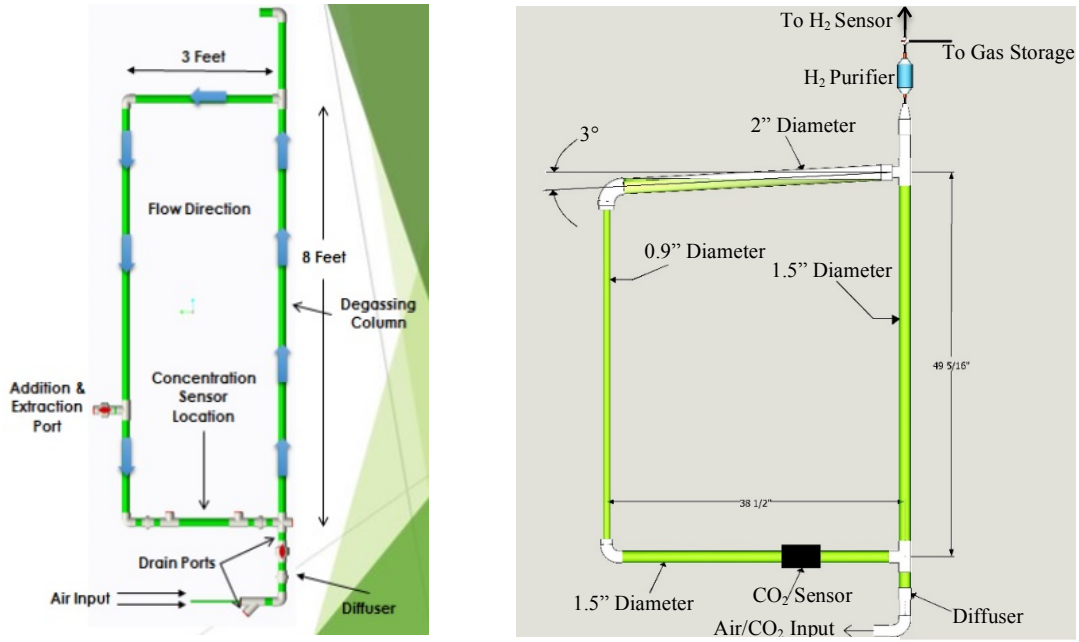


Fig 4: (a) Final design from 2014's Senior Team. (b) Current proposed design.

strain.

As photosynthesis occurs, hydrogen and small amounts of oxygen will be produced. It is therefore necessary to purify the hydrogen by removing the unwanted O_2. The purification will be done with an H_2 purifier, which can reduce oxygen, trace amounts of water, and organic compounds. At the outlet of the purifier the oxygen content will be 5ppm. Hydrogen purity less than 5ppm is beyond the scope of this project and should be done by an appropriate facility. The purifier has a ¼" fitting size and will be connected to the reactor via a 1.5" to 0.25" reducing PVC coupler. An airtight tee will be attached to the outlet of the purifier, which will divert the gas to the hydrogen sensor or the storage tanks. Some components of the proposed design will remain constant from the previous one. The CO_2 sensor will be used to make sure that the concentration does not exceed the amount required by the algae. The diffuser, air input, and drain ports will also be utilized in the proposed design as they are necessary. Detailed drawings of the current design can be seen in appendix A.

The sensor is a MQ-8 hydrogen gas sensor with a sensitivity of 100 – 10,000 ppm and is controlled through an Arduino Uno microcontroller board. The board has 14 digital input/output pins, 6 analog inputs, and a 16 MHz clock. The H_2 sensor and board requires programming and calibration for a correct readout. Figure 5 shows the prototype that has been assembled by the team in Brazil at UFPR. The system will operate on 5V with an input voltage of 7 – 12V, which will be supplied by an appropriate power adapter. When hydrogen is present, the system will alert the user through a chain of LEDs that light depending on the percent concentration, e.g. one LED for 5% concentration, two LEDs for 10% etc.

The hydrogen sensor will be placed within an airtight beaker with a sample of the algae being cultivated. As seen from the tests run at UFPR, if hydrogen is present, it will

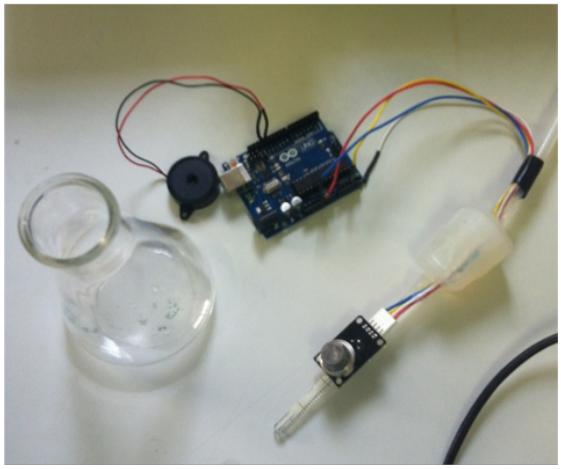


Fig 5: Prototype of H2 sensor system.

only take a few seconds for the alert programmed for the sensor to go off. The setup of the sensor within the beaker can be seen in figure 6. The sensor is programmed to continuously sense a concentration of H_2, but a constant reading will be unnecessary. If regular checks show hydrogen present, we are able to assume a constant hydrogen production. The full hydrogen sensor program code and dimension drawings can be seen in Appendix B.

Hydrogen can be stored as a gas, a liquid, or a solid using a metal hydride. Gaseous hydrogen storage is the most common form and perhaps the simplest storage method. Hydrogen gas is usually stored in a cylinder tank around 150-200 bars and at a temperature of 298 K. Adversely, gaseous storage is limited by volume considerations as a result of hydrogen's low density. Storage at high pressures can increase the energy density of gaseous hydrogen. Even at high pressures, large volumes of storage space are required which lead to high material cost.

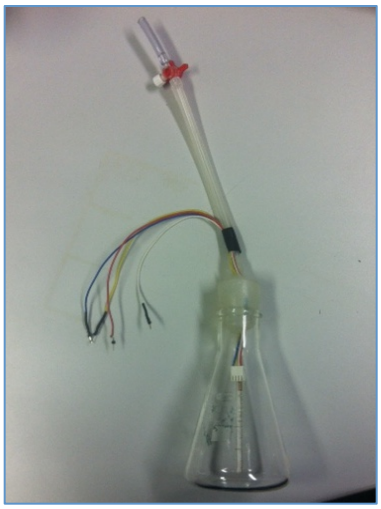


Fig 6: *Airtight beaker with sensor*.

Liquid hydrogen must be compressed more than gaseous hydrogen. The liquidification of hydrogen requires a large expenditure of energy, which may not be cost efficient. Liquid hydrogen is stored in cryogenic tanks. These tanks are usually spherical or cylindrical in shape in order to minimize surface area, which will also reduce heat transfer. In order to maintain its liquid form, it must be continually kept at a low temperature (i.e. less than 20 K). Cryogenic tanks are double walled with an evacuated layer of Perlite insulation to help sustain constant low temperatures. If the temperature of the liquid hydrogen rises too much, a high pressure could accumulate and result in damage or explosion. This is reflected by the high expansion ratio of liquid hydrogen to gaseous hydrogen.

Metal hydrides store hydrogen as a solid using some type of metal alloy. Hydrogen molecules are adsorbed into a metal matrix, which create a gas storage density that is higher than liquid hydrogen. Metal hydrides adsorb hydrogen at low temperatures and release the hydrogen when it is heated up. The need for heating and cooling requires that metal hydrides have additional control systems, which could be very expensive. Metal hydrides have the highest volumetric density and work well for restricted spaces. Although they store more hydrogen in a smaller space, they may not work well in systems that have weight restrictions.

B. Analysis

As mentioned above, physical properties of a reactor can influence light utilization of the algae and fluid properties such as gas holdup, superficial gas velocity, CO_2 mass transfer, and others. The surface area to volume ratio for tubular bioreactors is given as:

$$\frac{A}{V} = \frac{2\pi rl}{\pi r^2 l} = \frac{2}{r} = \frac{4}{d} \tag{1}$$

For the proposed design, the value of *d* used was the average diameter of 1.5 inches. Using equation (1) the area to volume ratio for the current proposed design is 2.67 in^{-1}. The higher the value for A/V the higher light utilization is. It should be noted that the value of A/V for this year's design is the same as 2014's design since it only depends on the diameter of pipe. Another important geometric property for bioreactors is the cross-sectional area ratio of the down-comer to riser. The area ratio is important for large-scale implementation as it shows a unit-less property of the reactor. The area ratio is calculated as:

$$\frac{Ad}{Ar} = \frac{\pi r_d^2}{\pi r_r^2} = \frac{r_d^2}{r_r^2} \tag{2}$$

The value of Ad/Ar for the proposed design was calculated as 0.36.

Along with light utilization, fluid properties can also influence the hydrogen output from the algae. Gas holdup is the volumetric gas fraction in a multiphase dispersion. It is calculated as:

$$\varepsilon = \frac{V_G}{V_G + V_L} \tag{3}$$

where V_G is the volume gas and V_L is the volume of liquid within the reactor. Gas holdup influences superficial gas velocity and the gas to liquid mass transfer [5]. Superficial gas velocity is the velocity of the gas bubbles that are

produced by the air pump and diffuser. Superficial gas velocity is crucial in the cultivation of algae within the bioreactor. If the gas bubble velocity is too high, the shear stress produced by the bubble can exceed the max shear stress of the algae strain and break it apart. Gas bubble velocity was calculated for *Chlamydomonas reinhardtii* strain using its max shear stress of 0.1 dyne/cm^2 or 0.01 Pa, which was determined from previous research [6]. No shear stress values were found for *scenedesmus sp* so the same gas bubble velocity determined from *Chlamydomonas reinhardtii* will be used. Using the shear stress value of 0.01 Pa and the equation for shear velocity:

$$v_{(shear)} = \sqrt{\frac{\tau}{\rho}} \tag{4}$$

where τ is the shear stress and ρ is the density of water or solution. From equation (4) the value of the shear velocity is 3.16 x 10^{-3} m/s. To determine the gas bubble velocity it was assumed that the shear velocity is 1/10th the mean flow velocity, and the velocity of the gas bubble was determined as 0.0316 m/s [7]. Next, the required gas volumetric flow rate of the pump was calculated using:

$$v_{gas} = \dot{V}_g / A_r \tag{5}$$

where A_r is the cross sectional area of the riser. The calculated volumetric air-flow rate of the pump is $3.61\text{x}10^{-5}\ \frac{\text{m}^3}{\text{s}}$.

Algae specimens require inorganic carbon in order to produce biomass. Inorganic carbon exists in various forms in liquid environments when the temperature and pH levels are right. Resistance to CO_2 diffusion can be a limiting factor during mass transfer [13]. The rate of mass transfer can be calculated from:

$$N_{CO2} = k_L a(C_{CO2}^{*} - C_{CO2}) \tag{6}$$

Where k_L is the liquid-phase mass transfer coefficient and a is the area available for mass transfer.

The net energy ratio (NER) is defined as the ratio of total energy produced in terms of biomass and hydrogen divided by the operation energy:

$$\text{NER} = \frac{\Sigma\ \text{Energy Produced}}{\Sigma\ Energy\ Input} \tag{7}$$

In order to make use of the hydrogen obtained from the microalgae, it must be purified, compressed, and stored. When hydrogen is initially collected from the bioreactor, there will be many other gases present such as oxygen, nitrogen, and carbon dioxide. A gas purifier is needed to obtain a more pure and usable form of hydrogen. For this project, an OxiClear inline gas purifier will be used. It has a maximum flow rate of 5 mL/min, an operating pressure of 5 psi to 125 psi and a fitting size of .25 in. This is smaller than the tube outlet of the bioreactor so a coupling must be installed. The purifier will be installed vertically to ensure satisfactory removal of contaminants. This specific purifier was chosen because of its high efficiency and low resistance to gas flow. Once the hydrogen gas has been purified it will then be compressed to an appropriate pressure based on the compressed tank used.

When hydrogen is stored, it does mechanical work and stores energy [13]. If hydrogen is treated like an ideal gas, the work needed for adiabatic compression of one mole of hydrogen can be found through the following equation:

$$W_{ad} = \int_{p_2}^{p_1} PdV = (p_1 v_1 - p_2 v_2)(r-1)^{-1} = R(T_1 - T_2)(\gamma - 1)^{-1} \tag{8}$$

Where:

- R is the gas constant
- P_1 is the pressure before compression, P_2 is the pressure after compression
- V_1 is the volume before compression, V_2 is the volume after compression
- T_1 is the temperature before compression, T_2 is the temperature after compression
- γ is the specific heat ratio: $\frac{C_p}{C_v}$

Treating hydrogen as an ideal gas will lead to error in volumetric calculations. In order for accurate solutions, hydrogen must be treated like a real gas. The discrepancy between the volume of ideal and real gas is solved using the compressibility factor Z [13]. The solution to this discrepancy is shown by adding Z in equation (9).

$$PV = nZRT \quad (9)$$

The compressibility factor Z is essential as the pressure increases and temperature decreases. The compressibility factor can be found by solving equation (10).

$$Z = 1 + p[A + BT^{-1} + CT^{-2} + DT^{-3} + ET^{-4}] \quad (10)$$

Where:

- p is the pressure
- T is the temperature
- A = $4.93482*10^{-5}$
- B = 2.04036
- C = 81.5334
- D = $-65561*10^{4}$
- E = $4.56516*10^{6}$

C. Evaluation of Designs

Hydrogen Storage

The final design selection was based on the following criteria: economic feasibility, safety, hydrogen storage capacity, minimal weight and size, ease of use, and the ability to undergo multiple charge and discharge cycles. The scoring breakdown for each criteria can be seen in the design matrix in table 1. Affordability, size, and storage capacity can be very closely related if there is a need for a mass amount of storage. For example, liquid storage in cryogenic tanks was given the highest score in affordability mostly because of its ability to store hydrogen with respect to its size. Even though compressed gaseous tanks of the same size are cheaper, they are not able to store the same amount of hydrogen as cryogenic tanks. For this project, large amounts of hydrogen are not expected so a gaseous compressed tank would be sufficient. Safety plays a huge role in determination of an appropriate hydrogen gas storage tank. Hydrogen is an extremely combustible gas so precautions must be made when handling it. The bioreactor design has been sized down for use in an indoor lab. Because of this, a hydrogen storage tank of a smaller size and weight would be most ideal. Another important determining factor is the ability of the storage system to undergo multiple charge and discharge cycles. The tank should be able to handle taking in hydrogen as well as releasing it an unlimited number of times. Additionally, the tank should be easy to use and require minimal operation in order to avoid additional maintenance.

Table 1: *Hydrogen Storage Decision Matrix*

Criteria	Hydrogen Storage Options		
	Gaseous	*Liquid*	*Solid*
Affordability	6	7	5
Safety	8	4	10
Storage Capacity	6	8	10
Small Size	7	7	9
Lightweight	6	8	3
Lifetime (number of cycles)	8	8	5
Ease of Use	10	5	4
Weighted Sum	**51**	**47**	**46**

Hydrogen Gas Sensor

One of the changes that will be made from the beginning of the semester is the sensor selection. At UFPR, the sensor currently being used is the MQ-4, which is able to detect several natural gases. The decision to change to the MQ-8 sensor was made by the fact that the new sensor only detects hydrogen gas. We hope this will lead to clearer and more precise readings. Challenges encountered so far will be with the lab production of hydrogen. The first strain used, scenedesmus, yielded no results and was unable to produce hydrogen. Once switching to the *Chlamydomonas reinhardtii* algae species, hydrogen was successfully produced.

D. Programming Needs and Control

Because this project focuses on the production of hydrogen, a hydrogen sensor is essential for determining if hydrogen is being produced. As stated previously, a MQ-8 sensor is being used because of its ability to detect

concentrations of hydrogen gas. The hydrogen sensor will be located immediately after the gas purifier outlet. Algae only produces hydrogen under specific conditions such as depriving it of nutrients like sulfur. The use of a hydrogen gas sensor will be helpful in determining how well the growth mediums are working and if any other options should be explored. The bioreactor is also in need of an automated continuous addition and extraction unit. This unit will replenish the bioreactor with nutrients and water as needed. It will also remove any dead algae. Without this addition and extraction unit, the bioreactor must be completely drained in order to remove dead algae and replace the bioreactor with a new growth medium and water. Completely draining the bioreactor could be very costly. An automated addition and extraction unit will increase the efficiency of the bioreactor and make it more marketable for large scale commercial use.

III. Risk and Reliability Assessment

A. Hydrogen Storage

The primary risks associated with this project involve the extraction of hydrogen. When hydrogen is mixed with gases like oxygen, it becomes flammable and explosive. In order to combat this potential safety threat, an additional sensor could be attached to the hydrogen storage tank to detect any leaks.

Many of the components were chosen based on their simplistic design. This allows for less maintenance and room for mechanical failure. The hydrogen gas purifier may have to be replaced overtime. After numerous uses, it may take more cycles to thoroughly refine the hydrogen gas.

B. Bioreactor

The primary risks associated with the bioreactor include leakage of hydrogen gas and the solution. The algae growth solutions contain a variety of chemicals, some of which may be harmful. It is imperative that proper precautions are taken in order to avoid any leaks and how to handle them if they occur. Hydrogen gas leaks are a huge risk and could be very dangerous. In order to combat this, a sensor could be used to alert the team of any possible leaks.

Because of the few mechanical components, there are very few issues related to reliability. To have an effectively working bioreactor, it needs constant light as well as circulation in order to agitate the algae. The primary mechanical component to this design is the air pump. This is a crucial part of the bioreactor design. The air pump circulates the water and algae through the bioreactor allowing light to spread more evenly amongst the algae. Because the gas purifier cannot be tested until the bioreactor system is put in use, the precision of hydrogen purity is only known based off of the values given by the manufacturing company. Depending on the efficiency of the purifier, it may take several cycles to achieve pure hydrogen gas.

C. Hydrogen Gas Sensor

There are no readily apparent risks associated with the sensor. However, there are many potential reliability issues that could occur. The sensor has only been tested on small-scale algae growth and hydrogen production in beakers. There may be error when it is used on the larger scale bioreactor. Issues with the addition and extraction unit may arise if it is unable to detect and effectively remove dead algae. If it is not able to add nutrients and fresh water to the system, the growth and health of the algae will be affected.

IV. PROCUREMENT

A. Purchase Orders

As of December 8, 2014 there have been three purchase orders completed. Items ordered include the microalgae to be grown, two species were ordered in a single purchase order, and the nutrient media solutions needed to promote growth of the algae, both of these solutions were obtained a separate purchase order. Items ordered may be seen in table 2. The other purchase orders will be completed no later than December 12, 2014 and items in the purchase order list will include items listed in the budget under the Project Management section of this report.

Table 2: *Purchase Orders*

Item	Quantity	Cost ($)
Scenedesmus Living / 152510	1	6.66
Chlamydomonas reinhardtii / 152040	1	9.86
Bold Basal 500 mL Solution / B5282-500mL	1	38.9
TAP Growth media Chlamydomonas / A1379801	1	37.5
Total		92.92

V. COMMUNICATIONS

One of the biggest challenges associated with this project has been communication. Half of the team members are studying abroad at the Federal University of Parana in Brazil while the remaining group members are located at Florida State University in Tallahassee, Florida. The Brazil team's access to internet is very limited which has required everyone to be very organized and communicate effectively during video conference and emails. To accommodate varying schedules, email has been the primary form of communication. Video conferencing has been used to supplement emails and provide an opportunity for all team members to ask more questions and receive detailed responses. Communication with the sponsor has occurred through email as well as regular meetings.

VI. ENVIRONMENTAL AND SAFETY ISSUES AND ETHICS

A. *Hydrogen*

Hydrogen is a flammable gas that can ignite over a very wide range of combustible concentrations in air, between 4% to 75%. Compared to gasoline, propane, and natural gases this is a very wide range as shown in figure 7 [14]. Furthermore, this gas requires very low ignition energy to ignite − about one-tenth of the energy needed to ignite gasoline vapors − so a lit cigarette, or even a spark released from a person with an excess of static electricity, can cause hydrogen gas to ignite at its stoichiometric fuel-air mixture of 29% [15]. Hydrogen gas burns at a temperature of 3,713 □F (verses 2,276 □F for gasoline) but radiates little infrared heat, and no smoke, making inadvertent contact with the flame a strong possibility [16]. It does, however, emit significant amounts of ultraviolet radiation which can be dangerous should overexposure occur [14]. Also, the flame is almost undetectable by the human eye making detection measures a high priority to avoid the hazard presented by the ignited gas.

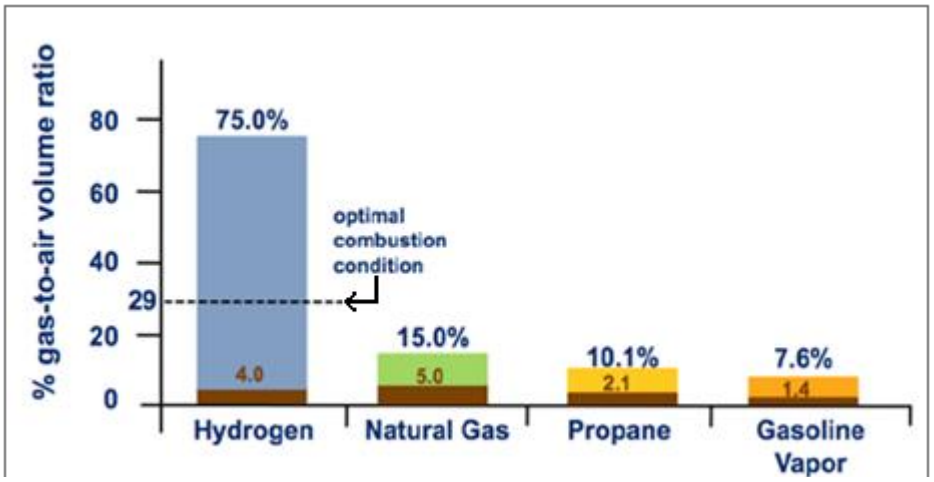


Fig 7: *Gas to Air Volume Ratio*

Not only is hydrogen gas flammable, like any other gas it has the potential to explode as well. A hydrogen cloud that grows as a result of a leak in a confined space,

or the accumulation of gas in a covered area outdoors, produces an explosion hazard. Flames can spread through the cloud at a velocity of several meters per second, and when the fuel is detonated in a closed area it can create an increase, of almost eight times, in the pre-explosion pressure [14] [15]. Should the detonation occur in a tank of hydrogen the pressure increase would happen so quickly that devices designed to relieve pressure become obsolete [15]. Furthermore, the pressure could increase to a point that is high enough to explode buildings which could cause even more catastrophic damage. Detonation of hydrogen gas can also occur over a wide variety of mixtures, ranging from 18.3% - 59% [15].

Due to the low viscosity, buoyancy, diffusivity, and molecular size of hydrogen gas it is difficult to contain, therefore, this gas is prone to leaks 15]. Not only can these leaks create a combustible situation, it can also create an environment that is harmful to respiration. In a smaller confined space, all gases (except oxygen of course) may cause asphyxiation, and even though this may be rare due to its physical properties, it is still a possibility [15]. The possibility of a jet stream forming that extends meters poses an even greater threat; should the stream ignite it could cause serious damage to anything in the path of the jet flame or in the blast radius should an explosion occur [14].

B. *Microalgae and Constituents*

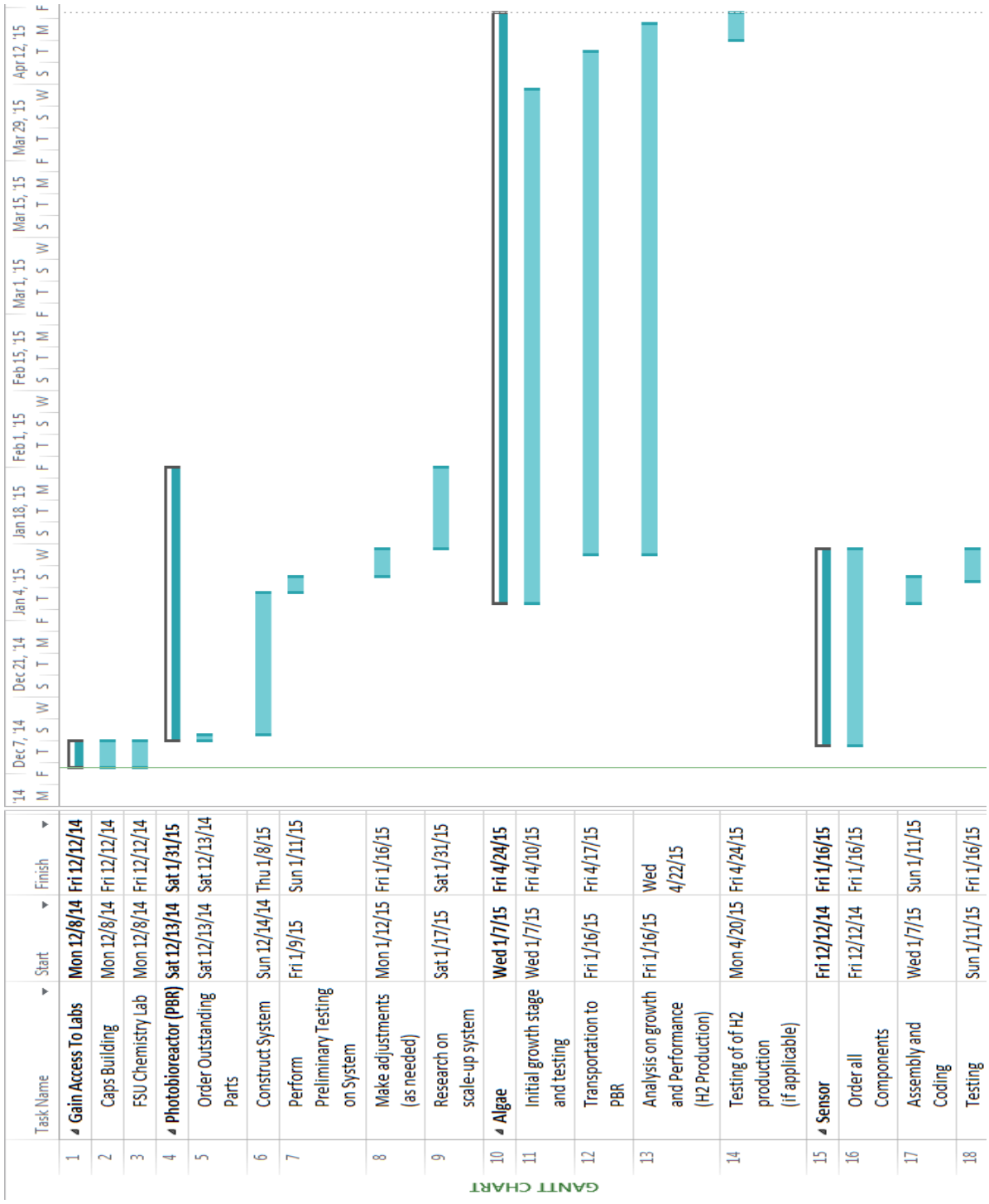
When growing microalgae a media rich in various nutrients must be used; these nutrients include, nitrogen, potassium, and phosphorous, among many others. The photobioreactor must be expunged of this media (and the microalgae) at the end of the organism's life cycle. Casually disposing of the algae and the nutrient rich water that it grows in, into the sewage or other aquatic outlets can have negative effects on the environment. Disposing of the growth media into other waterways can create nutrient dense marine environments that promote the growth of other strains of algae [16].

This "algae bloom" can have several effects on the biodiversity such as the increase in toxicity of the water. Various types of algae produce toxins that harm the water supply so human and animal exposure to these toxins is dangerous and can lead to various health problems or even death; more and more incidents of the effects of this algae toxicity are being reported [16].

Not only is the toxicity a major issues when it comes to environmental and safety issues, but so is the chemical reactions that occur as a result of the presence of dying algae or the components of the media that is grew in. For instance, as algae decays they release nitrogen and phosphorous, but also consume oxygen from the water source [17]. Nitrogen and phosphorous assist in the growth of new algae and can lead to undesirable levels of toxins that may poison people, wildlife, and other creatures of the environment. The low levels of oxygen lead to fish kills in which large amounts of fish die due to a lack of oxygen supply in the water [17]. Also, depending on the solution, if it is copper enriched, the copper in the solution will form a new toxin in the water (copper carbonate) that will interfere with certain bacteria decomposition which could negatively affect the breakdown of sewage [17]. Furthermore, parasites may grow in the water where the algae is disposed of due to a spike in pH levels caused by the growth of algae in an unnatural and uncontrolled environment [18]. In order to counteract the environmental and safety issues associated with the disposal of dead microalgae close attention must be paid to how and where it is discarded.

VII. PROJECT MANAGEMENT

A. Gantt Chart



B. Budget

This design project was funded $1,000 by the FAMU-FSU College of Engineering. Of this budget $92.92 has been spent on the purchase orders listed in the Procurement section of this report. Table 3 shows a breakdown of how the budget will be spent for the duration of the senior design project while allowing room for error.

Table 3: *Budget Breakdown*

Item	Quantity	Cost (per item, $)	Cost (total, $)
Scenedesmus Living / 152510	1	6.66	6.66
Chlamydomonas reinhardtii / 152040	1	9.86	9.86
Bold Basal 500 mL Solution / B5282-500mL	1	38.9	38.9
TAP Growth media Chlamydomonas / A1379801	1	37.5	37.5
Distilled Water Gallons	5	1	5
Compressed Hydrogen Storage Tank	1	300	300
Fluorescent Lighting	5	9.97	49.85
OxiClear Filter	1	265	265
4' x 1'' Clear PVC Pipe	1	12.16	12.16
4' x 2'' Clear PVC Pipe	1	36.94	36.94
1.5'' Wye (Addition Port)	1	5.38	5.38
2'' 90° PVC Elbow	1	1.82	1.82
1.5'' PVC Tee	1	1.54	1.54
2'' Male to 1'' Female Reducing Bushing	1	1.57	1.57
1.5'' Male to 1'' Female Reducing Bushing	1	0.95	0.95
2'' Male to 1.5'' Female Reducing Bushing	1	1.57	1.57
1.5'' Male to .5'' Female Reducing Bushing	1	0.95	0.95
Total			775.65

C. Resource Allocation

Fall semester, the UFPR team started with initial experiments with growing algae and testing different growth mediums. These mediums were created onsite. They tested different ratios of sulfur and other essential nutrients to examine how algae growth and hydrogen production was affected. UFPR also worked on programming and calibrating a hydrogen gas sensor to determine the concentration of hydrogen gas produced

by the algae. Both tasks were completed over the course of the entire fall semester. The FSU team ordered materials such as algae growth mediums as well as both algae species, *Chlamydomonas reinhardtii* and *scenedesmus sp.* Over the course of the fall semester, the FSU team focused on calculations in order to derive the mass flow rate necessary to agitate the algae in the bioreactor without causing harm to the cell membranes. This was needed to ensure that the bioreactor could still use the air pump from last year's project. Along with this, several major changes were made to the bioreactor design.

Spring semester, team members studying in Brazil will be back at FSU. Spring semester will be dedicated to growing and maintaining algae in the bioreactor. Experimentation with growth medium solutions will continue to take place during the first month of spring semester. Along with this, different types of water will also be tested. This will be done in hopes of finding the best solution in order to maximize algae and hydrogen production. Once enough algae is grown and a suitable growth medium is determined, the algae and solution will be moved into the bioreactor. This is expected to occur sometime in February. Once moved to the bioreactor, it may take up to two weeks for the hydrogen gas sensor to detect a significant amount of hydrogen. Once hydrogen is detected it will then be stored into a compressed hydrogen gas tank. An addition and extraction unit will also be underwork during the entire spring semester. Because of the complexity in creating an automated continuous system, it is expected to take 2 to 2.5 months to complete the unit.

VIII. FUTURE PLANS FOR PROTOTYPE

The current design of our photobioreactor system is developed to work for a small amount of microalgae when considering this idea at the plant-sized level. In order to scale up our system a few things must be taken into account. These include:

- *The type and set up of a photobioreactor system*

  The airlift type PBR that we will utilize in our design is not the ideal kind for a hydrogen producing PBR on a more grand level. Our model is more so vertical in nature as opposed to horizontal, which proves to be an issue when trying to scale up the system. The greater the height of the photobioreactor, the greater the distance that gas bubbles must travel in order to be captured. However, the increased height and pressure will slow down the rate at which hydrogen gas bubbles will diffuse and increases the potential for them to be consumed by the microalgae which will decrease hydrogen productivity [19]. A proposed system for future large-scale use will more than likely be as horizontal as possible to hinder this effect, but will have a slight tilt as in our design now that will assist in the cultivation of the gases produced.

  Lighting is another proponent that will be addressed in terms of scaling up the design. One of the desirable characteristics about microalgae is that it is photosynthetic and can use the energy of the sun, which is essentially in abundance, to synthesize the hydrogen gas that we desire. Therefore, placing a system on the plant sized scale outside to bask in the sunlight is a very desirable idea. This energy is free and will keep the costs of lighting the system at a minimum. However, at night time it would be ideal to implement an artificial light source either inside or outside of the photobioreactor to keep the rate of production of hydrogen as constant as possible.

  By keeping a high surface-to-volume ratio as we do in our photobioreactor we can hinder the self-shading effect that would exist at smaller ratios. This will hinder the blocking of light intensity by the cells closest to the surface of the PBR. Adding lights directly inside of the system is another way to combat this issue but is more elaborate [19].

- *Creating a more continuous system with automatic addition and extraction of gases and biomass and nutrients*

  Our current system is not a continuous photobioreactor system since our primary focus is the production of hydrogen gas from the two specific strains of algae stated earlier. However, implementation of a continuous system in which microalgae and nutrients are added in while gases and/or dying algae are removed at the most opportune time is ideal. More research has to be done in order to insist ways in which to implement a design of this nature.

- *Disposal and recycling methods*

When disposing of algae several factors come into play including its toxicity to people and other animals and wildlife. Therefore, it is suggested that samples of each batch be sent to a lab for diagnostic as to its contents and how detrimental discarding the algae to the natural environment would be. However, since the growth media will still be loaded with the necessary nutrients to promote algal cell growth up the death of previous cells it is attractive to find a filtration system that will remove the dead algal cells in order to reuse the existing water of from the system. This idea would cut down on the costs of the water and nutrients needed for this process that must be purchased. It will also limit the environmental damage that expelling the obsolete algae into our ecosystem would bring about on, especially on such a large scale.

- *Safety precautions*

As stated above there are various safety precautions that must be considered when working with hydrogen gas, especially when the gas is compressed. Aside from always wearing personal protective equipment (PPE), it is advised that a training course be mandated when implementing the design for the photobioreactor on a large-scale. This course should cover emergency related information pertaining to leaks of hydrogen gas. Furthermore, sensors to detect the hydrogen gas would need to be implemented in the design of a photobioreactor plant seeing as how this is a colorless, odorless, and tasteless gas that would otherwise go undetected by the senses of people. Odorants are ineffective seeing as how the hydrogen gas molecules are so small that odorants fail to travel fast enough to give a warning when a dangerous amount of the gas is present [14].

IX. CONCLUSIONS

The continuous development of renewable energy sources like that of hydrogen can make a positive impact on society. Decreasing society's dependency on fossil fuels will not only create a cleaner atmosphere by reducing greenhouse gas emission, but it is also an economically viable energy option. This design project is focused on developing a more efficient way of cultivating microalgae as well as maximizing the amount of hydrogen that is produced and extracted in order to develop an effective energy alternative. The design will incorporate a photobioreactor, hydrogen gas purifier, hydrogen gas sensor, and storage. Due to budget and time constraints it was necessary to use the prototype from the 2014 senior design team. This design was chosen because of its simplicity and the fact that it is an airlift bioreactor, which has the advantages of good mixing, effective mass transfer of CO_2, high S/V ratio, and good removal of O_2. However, several modifications had to be made so that the photobioreactor could be optimized for hydrogen gas output. Two important characteristics of the proposed design include the surface area to volume ratio and the cross sectional area ratio between the down-comer and riser with values of 2.67 in^{-1} and 0.36, respectively. It was also necessary to calculate the maximum velocity of the gas bubbles produced so that the shear stress the algae are subjected to does not break them up apart. The max mean bubble velocity calculated in this case was 0.0316 m/s.

The hydrogen gas sensor that will used is an MQ-4 hydrogen gas sensor with a sensitivity of 100 – 10,000 ppm and is controlled through an Arduino Uno microcontroller board. A prototype of the sensor has been built and programmed at UFPR. However, the sensor must be rebuilt, tested, and calibrated at Florida State University. When hydrogen is present, the system will alert the user through a chain of LEDs that light depending on the percent concentration, e.g. one LED for 5% concentration, two LEDs for 10% etc. The hydrogen output of each strain, Scenedesmus sp. and Chlamydomonas Reinhardti, will be calculated from the percent concentration, the total volume of the beaker, the total volume of the algae cultivated, and the time needed to reach the percent concentration detected. Large-scale implementation of the proposed design will be looked into during the spring semester.

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APPENDIX A

CAD Drawings for Photobioreactor

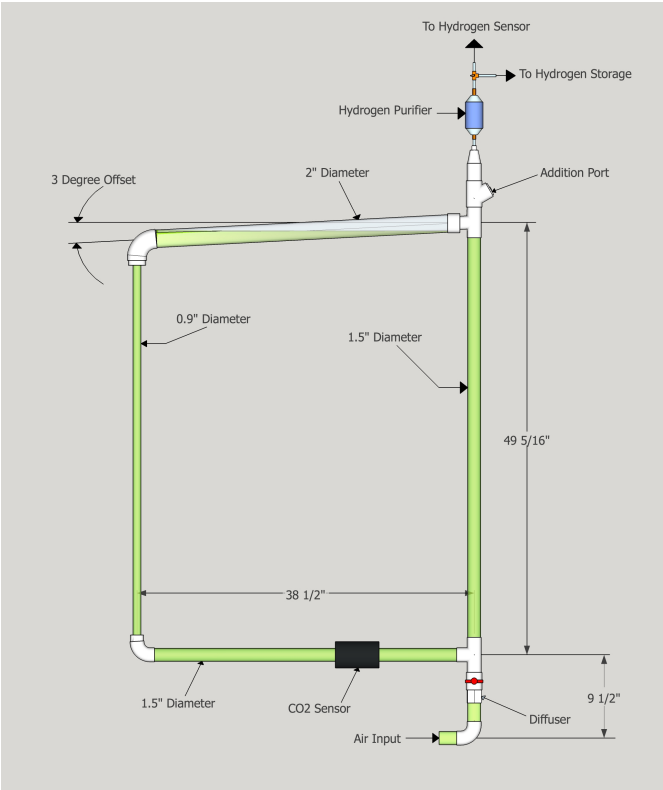


Fig 1A: Front view of photobioreactor with dimension

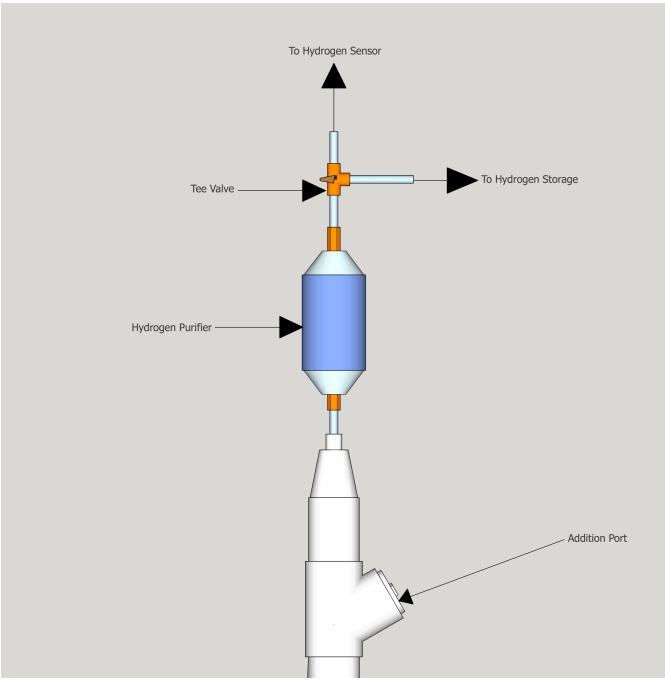


Fig 2A: Components and connection of degasing column.

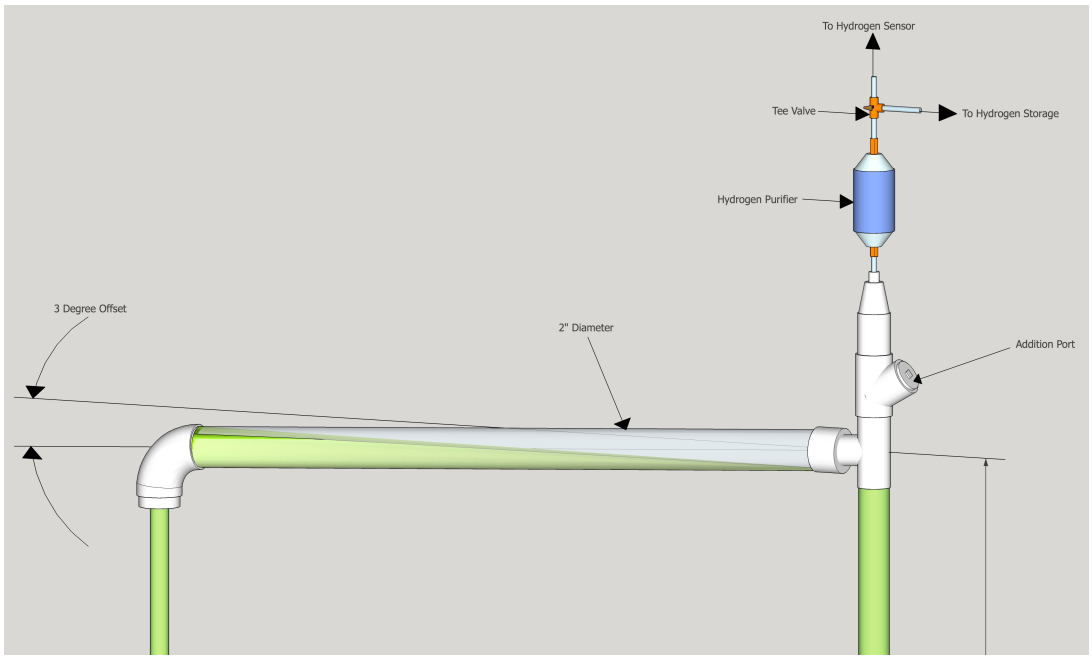


Fig 3A: Top half of photobioreactor.

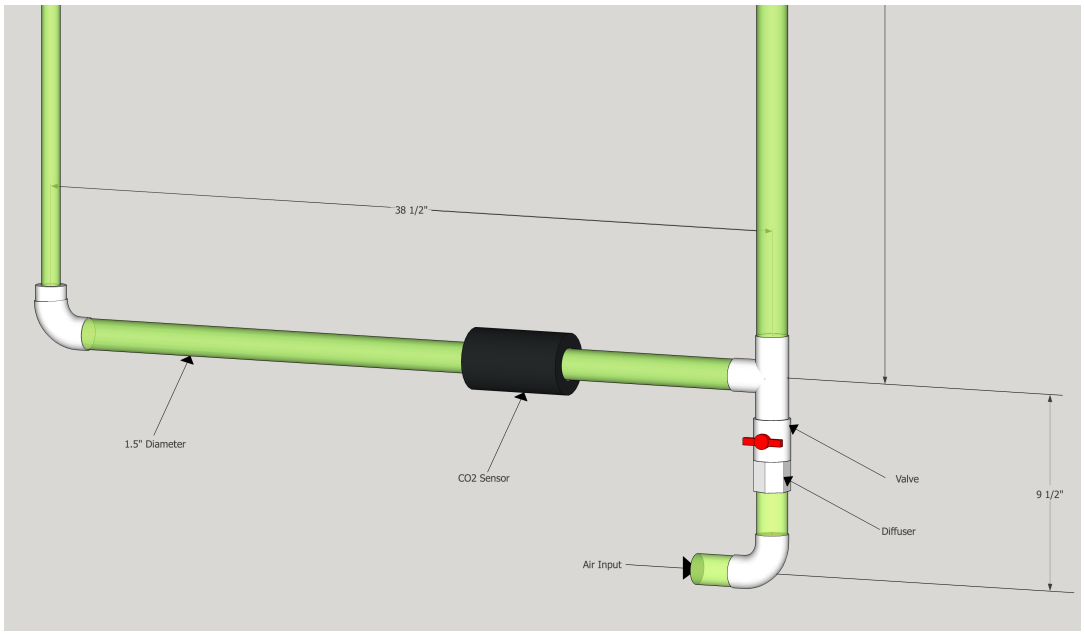
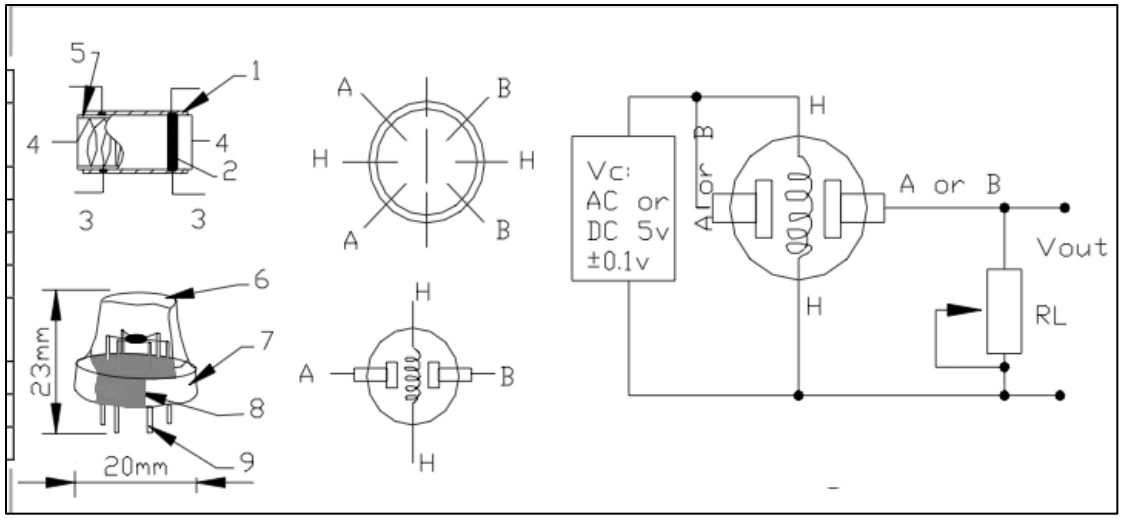
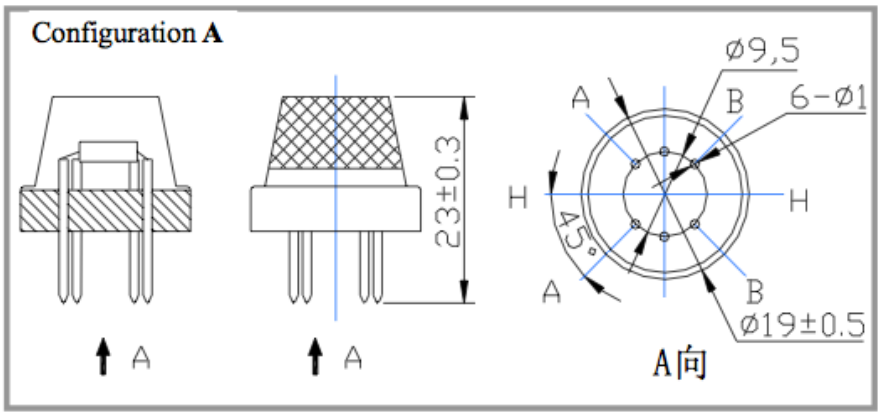


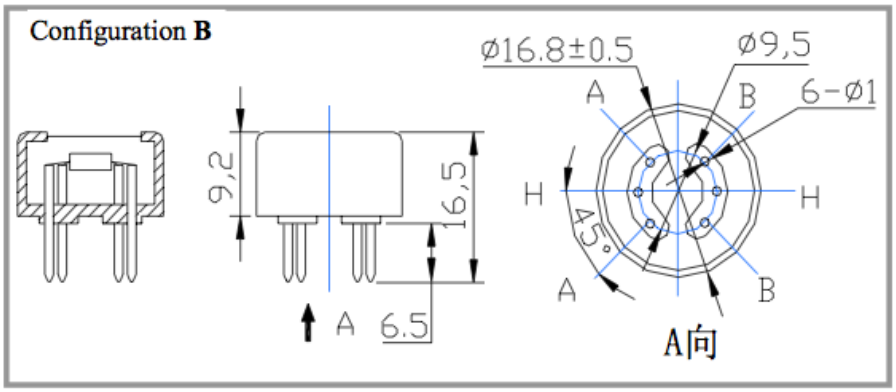
Fig 4A: Top half of photobioreactor.

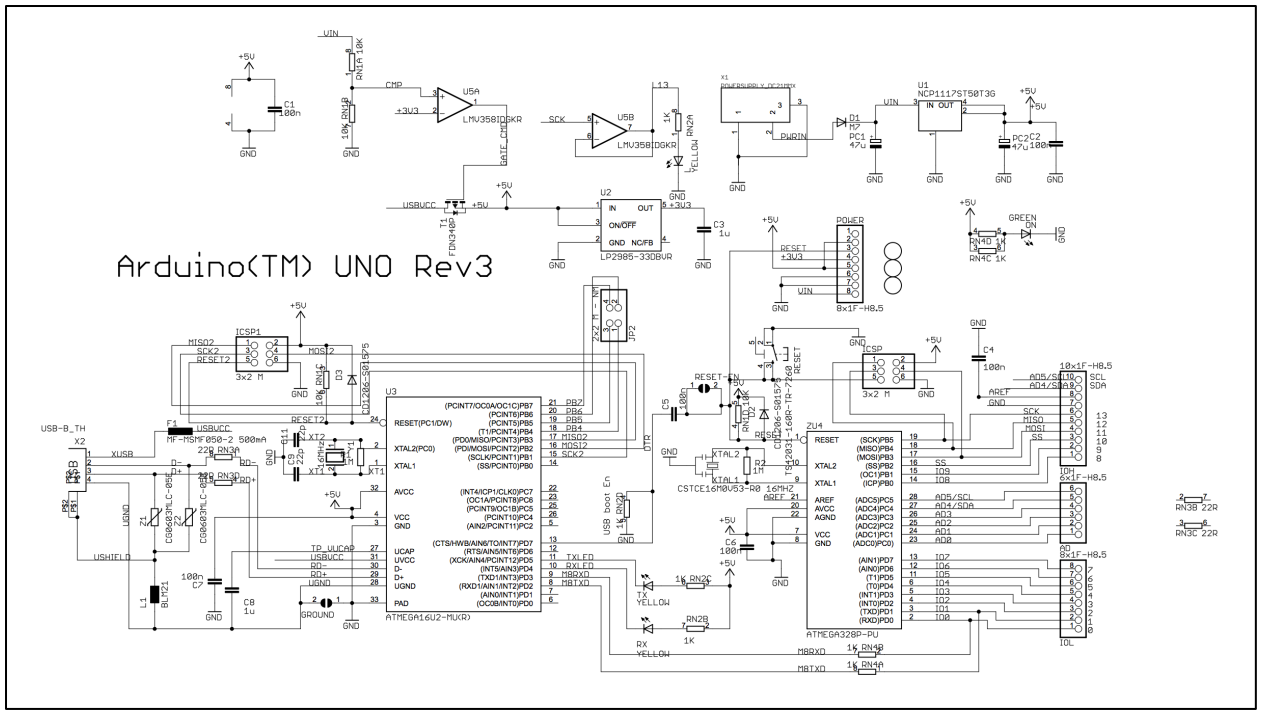
APPENDIX B

Hydrogen sensor Drawings and Program Code









Testing Program Code for Hydrogen Sensor

```
void setup()
{
SOM[1]=13;
pinMode(SOM[1], OUTPUT);
//Serial.begin(9600);  // sets the serial port to 9600
}
void loop()
{
  digitalWrite(13,LOW);
  delay(100); //Delay para efeito de blink do LED, indicado que o teste pode ser feito pelo usu·rio
  int sensor = analogRead(sensorPin); //LÍ o sensor e guarda na vari·vel
  if(sensor >= 250) //Se a leitura for maior que 40 (valor escolhido para a demonstraÁ„o utilizando-se um
antissÈptico bucal)
  {
    digitalWrite(13, HIGH); //Acende o LED Azul(Indicando que o sensor detectou um mÌnimo de ·lcool (sensor >=
40)
    delay(2000);
    }

  //sensorValue = analogRead(sensorPin);       // read analog input from sensor pin
```

```
  //Serial.println(sensorValue, DEC);  // prints the value read
  //delay(2000);                       // wait 2000ms for next reading
}
```

Full Hydrogen Sensor Program Code

```
// Code to sense hydrogen levels
// Arduino Board UNO
// MQ-8 Hydrogen Gas Sensor that uses 5V
// 3 LED lights
int LED1 = 1;
int LED2 = 2;
int LED3 = 3;
void setup() {
  // put your setup code here, to run once:
  for (int thisPin = 2; thisPin < 5; thisPin++)  {
    pinMode(thisPin, OUTPUT);
  }
}
void loop() {
  // put your main code here, to run repeatedly:
  // loop from the lowest pin to the highest:
  for (int thisPin = 2; thisPin < 5; thisPin++) {
    // turn the pin on:
    digitalWrite(thisPin, HIGH);
    delay(timer);
    // turn the pin off:
    digitalWrite(thisPin, LOW);
  }

  // loop from the highest pin to the lowest:
  for (int thisPin = 4; thisPin >= 2; thisPin--) {
    // turn the pin on:
    digitalWrite(thisPin, HIGH);
    delay(timer);
    // turn the pin off:
    digitalWrite(thisPin, LOW);
  }}/* FOR sensor ? then LED!
```