Introduction

The production of biofuels has been a tempting subject for experiment dating as far back as the Ford model T. The development of a biofuel product has been sparked with intensity within the last thirty years, due largely to the known fact that the depletion of fossil fuels is inevitable. Knowing this, many countries have been and are continuing to develop a cost efficient sustainable fuel source to take the place of petroleum. This will hopefully lead to a decrease in the pollution and an extended life for some of the earth's important fossil fuels.

In the year 1975 Brazil made major progress in the production of biofuel. The same year Brazil developed an ethanol motor fuel program largely dependent on Sao Palo Sugar Cane Industry. It was reported that 56% of the year's sugar cane crop was put towards the development of this ethanol program. This significant step in the development process of an efficient biofuel has recently led to the merger between an Italian Energy Company Eni and Brazil's national oil company, facilitating the export of Brazilian biofuel to Italy (http://www.shana.ir/109704-en.html).

More than two decades later, President Bill Clinton made his contribution to propel the United States into a biofuel oriented country. President Clinton presented a federal campaign that promoted the use of biofuels in creating energy and fuel sources. With the creation of this federal campaign President Clinton had the intention of tripling the use of biofuels by the United States in the year 2010. President Clinton's strive towards tripling the United States biofuel use from 1999 to 2010 was successful. He sparked the idea in the minds of government officials to implement initiatives to further maximize the use of biofuels within the US. These initiatives consist of; mandating biodiesel purchases, a subsidy-like bio-energy program and lastly a goal oriented order to displace 20% of current mobile fuel usage up to and through the year 2010. Kudos to these presidential and government decrees, the US is currently the largest producer of ethanol which is a cheaper alternative to petroleum, used to power cars. Along with the production of petroleum the US is also navigating its way through the areas of hydrogen, and butanol biofuels and microbial fuel cell production (ProQuest Archiver).

In order to assess the current state of technological advancement with respect to producing ethanol or butanol, it is essential to look at the invention of individuals and companies that are patenting products and processes. Later in this report, four patents that show some advancement in the production of butanol and/or ethanol will be evaluated along with patents that show hydrogen is a viable option, and patents that highlight relevant advances in MFC's.

Patents, disclosed proprietary information can be researched on the United States Patent and Trademark Office website in two forms of documents. Applications signify the newest forms of technology in a given area, although the claims that these companies make have not been extensively reviewed. Furthermore, the specifications of the invention or process are not required on the application as a form of security for the company until the patent is confirmed. Patents are also filed for the invention of new process pathways, production plant ideas, and other inventions regarding aspects including bacteria strain development.

The first chapter being discussed concentrates largely on the production of ethanol and butanol by way of lignocellulose material. Ethanol (ethyl alcohol), the same type of alcohol found in alcoholic beverages, is mainly used as a biofuel additive for gasoline (wikipedia). Butanol can also be used as a fuel source. Its longer hydrocarbon chain causes it to be fairly non-polar; it is also more similar to gasoline than it is to ethanol (wikipedia). Ethanol and Butanol can also be produced from various feed stocks most of them containing starch. As mentioned above one feedstock primarily being researched is referred to as lingocellulosic material. This material contains plant biomass composed of cellulose, hemicelluloses and lignin. The lignocellulosic material needs to be pretreated in order to break it down into simple monomers of glucose which can then be fed to the bacteria. Starch is used to feed the bacteria that produce this lingo cellulosic material. One the patents described in this report used a process of depolymerizing to convert lignocellulosic material to simple sugars and then to butanol.

The next chapter discusses the possibility of using hydrogen as a viable substitution for all our petroleum needs. As fossil fuels and natural gas begin to disappear, scientists are looking towards hydrogen as a solution to supply their energy needs even more. Presently the world is in a hydrocarbon economy and hydrogen is suggested to solve all the negative aspects of it. Advocates of hydrogen claim that it can be used as a cleaner more efficient alternative to fossil fuels as well as decrease their demand.

Hydrogen Production is one of the main problems in the use of hydrogen as a fuel. The current method of production, using fossil fuels to create hydrogen produces greenhouse gasses and is not sustainable for future use. Microorganisms are being looked at as a way to better produce Hydrogen. Anaerobic microbial cells that have the ability to produce hydrogen in an amount that could be industrially useful can be a big help to our hydrogen needs. The use of hydrogen producing microbial could be a way to create a cleaner energy source

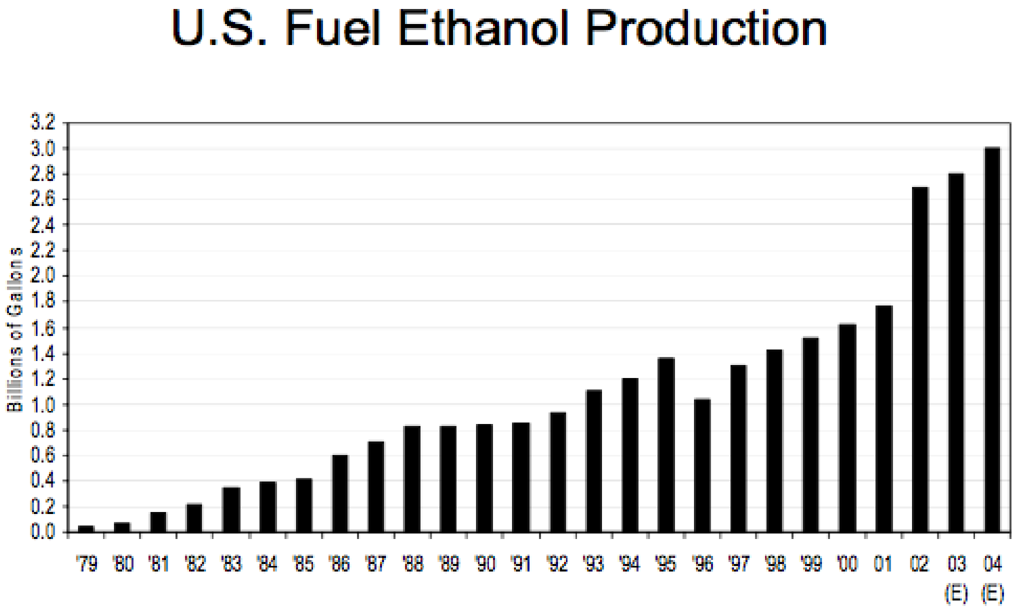
Then final chapter being discussed contains information to the development of technology concerning the microbial fuel cell. The basic operation of MFC is to use bacteria to harness electrical power. The microbial fuel cell (MFC) has been around for decades. Within the last decade significant advances have been made which allow them to be commercialized for waste water treatment.

A specific invention concerning MFC’s is the benthic (a collection of organisms at the bottom of a body of water) microbial fuel cell which allows a simplified layout for underwater applications. These can be utilized in oceans or rivers and can be deployed for years in low power sensor platforms. This process is specifically designed to power sensor systems, such as seismic sensors. Rather than relying on cultures of bacteria incubated on to the anodes, the benthic MFC utilizes the microbes found in the sediment within the water to generate its power.

Biofuels are the key to a greener universe independent of petroleum. The possible avenues through which research can be conducted are; butanol, ethanol, hydrogen and MFC. These all have promising attributes propelling them forward towards the invention of an efficient biofuel. In further reading of this report, you will begin to understand in detail the technological advances being made with respect to each individual avenue.

Chapter 2 Ethanol and Butanol

Ethanol and butanol, alcohols with two and four carbon atoms respectively, have been strongly considered as fuel sources for various applications. The production of ethanol in the United States has increased steadily over the last thirty years due to the recognition that dependence on foreign oil and energy is a significant threat to national security.



(E) Ethanol production estimated based on year-to-date production from U.S. EIA

Figure 2.1 (California Energy Commission, 2004)

Interest in butanol production as an alternative fuel source has also started to grow in the United States, and only recently has the idea started to become feasible. Although ethanol and butanol contain less BTUs, a measurement of the potential power of a particular fuel, than gasoline per unit of volume, their use as a fuel source is advantageous in many other factors. Over the last thirty years, the market has created a strong focus around ethanol, which has subsequently pushed butanol production onto the back burner. Ethanol is currently dominant in production and is fermented in the United States from corn crops, although other starch-based crops can be used in the microbial process with similar strains of yeast. Butanol is produced most effectively from the use of engineered microbes, which also consume a variety of biomass.

	Gasoline	Ethanol	Butanol
Chemical Formula	C_6H_{14} and $C_{12}H_{26}$	C_2H_5OH	C_4H_9OH
Composition by Weight	85-88% Carbon 12-15% Hydrogen 0% Oxygen	52.2% Carbon 13.1% Hydrogen 34.7% Oxygen	64.9% Carbon 13.5% Hydrogen 21.6% Oxygen
Reid Vapor Pressure	4.5 psi	2 psi	.33 psi
BTUs	115,000 BTU	105,000 BTU	75,700-84,000 BTU

Table 2.1

An analysis of the table above shows specific properties of gasoline, butanol and ethanol can be found be found below:

- While the energy output from Gasoline is the highest, Ethanol and Butanol still contain enough power to supply a combustion engine. Butanol contains 95.65% of the potential power that gasoline contains, while ethanol contains 73.04%. Gasoline fueled appliances are designed to withstand certain pressures and forces, which means that an alternative energy would have properties that are similar to gasoline, or contain a more advantageous factor then gasoline when used in gasoline powered appliances. With respect to this specific property, butanol is a closer match to gasoline than ethanol.
- Ethanol has corrosive qualities, which prohibit its transportation through existing gas lines. This quality also forces ethanol to be used as an additive to gasoline, rather than a replacement. Concentrated amounts used in an automotive engine would deteriorate pipelines within the engine. Modification of pipelines and engines would be required in order to utilize it as an alternative fuel source. Gasoline and butanol are not prohibited from use in existing pipelines.
- Evaporative qualities of the three fuels can be measured by the reid vapor pressure. Lower reid values suggest a substance that is less evaporative than a substance with a higher reid value. The reid vapor pressure of gasoline, ethanol, and butanol are 4.5 psi, 2 psi, and .33 psi respectively. The data suggest that butanol would be the safest for transport and handling, but

the low vapor pressure could result in problems when used in engines that were cold. Current gasoline engines utilize a device called sparkplugs which ignite a spark within the cylinder, causing gasoline vapors to explode and the resulting gas in the chamber to explode. Low vapor pressure, would be even less evaporative in a cold engine, might cause an inability of sparkplugs to explode the gas within the chambers. A possible alternative to the solution might be to use diesel engines which use compression to explode the fuel source as opposed to a spark. In either way butanol seems to be a more appropriate replacement in entirety to gasoline.

Ethanol fermentation is an old process that outdates the production of butanol by hundreds if not thousands of years. Its use as a fuel source began only in the 19th century, prior to which it was used to make alcoholic beverages such as wine, beer, and some higher concentration drinks. For the latter of the 19th century, ethanol was used as a lamp fuel, and experimented with as a fuel source, but taxes levied onto it would restrict its commercial use until 1906 when the tax was repealed. In 1908, Ford Motor Company designed the first engine to run solely on ethanol, derived at the time from corn. After World War I, the United States entered the era of prohibition, in which ethanol was made illegal to consume. Fuel producers were accused of a allying themselves with moonshine producers, and the result was a halt in the production of alcohol. Furthermore, the price of gasoline was so low moving into the 1940s and 1950s that there was no demand for ethanol as a fuel source. Major consumption of ethanol fuel would only resume after its use as an additive to gasoline for the purpose of oxygenation in the late 1980’s. Ethyl Tertiary Butyl Ether, derived from ethanol, and MTBE (Methyl Tertiary Butyl Ether), which was derived from a chemical process using methanol and isobutylene, were used to achieve this oxygenation. In the Late 1990s, a ban was placed in many states on MTBE, because of its tendency to seep through the ground and pollute the drinking water of cities. The ban on MTBE allowed for a greater focus on ethanol production that dramatically increased at the early start of the 21st century.

Although Acetone, Butanol, and Ethanol (ABE) fermentation was invented by Louie Pasture in 1861, it was not until the early 1900s that it reached an industrial level of production during the First World War. Butanol was considered to be an unwanted by-product of fermentation. During the First World War, Acetone was produced to aid the production of cordite, smokeless gunpowder that was used in .303

British rifles. The fermentation process yielded roughly twice the amount of butanol as it yielded acetone, which was consequently stored away in facilities until after the war was over. Later it was found that adding cotton nitrate to butanol produced a lacquer that was immediately implemented into the automotive industry to give paints a glassy look. This time period also marked creation of synthetic rubber, due in part to the rising price of natural rubber. Butanol was a key component in the production of synthetic rubber, which escalated production demands. In between the First and Second World War, the low price of molasses made it viable as a feedstock additive that increased fermentation yields while reducing the production costs. Molasses was mixed into grain mash in order to create a feedstock for AB producing bacteria strains. During this time, the process became international with many countries finding the production of the two alcohols to be a profitable venture when sold to European countries. Various fermentation plants were created in countries like South Africa, India, Egypt, Australia, the USSR, Canada, and the United States. AB fermentation dramatically decreased in 1950 when the price of petrochemicals, which could also be used to make Butanol and Acetone from an inorganic pathway, became more cost effective. In coordination with the production of low cost petrochemicals was an increase in the cost of molasses. This rise in price was due to its adoption by cattle farmers as an additive into cattle feed which subsequently created a larger demand for the product. By the 1960's AB fermentation ceased to exist. It has only been in more recent years that AB fermentation has been reopened as a possibility for industrial production. Rises in fossil fuel prices coupled with concern for environmental impact and our carbon footprint pushed the scientist and researchers to look for alternative fuel possibilities, including the strong consideration of butanol and ethanol.

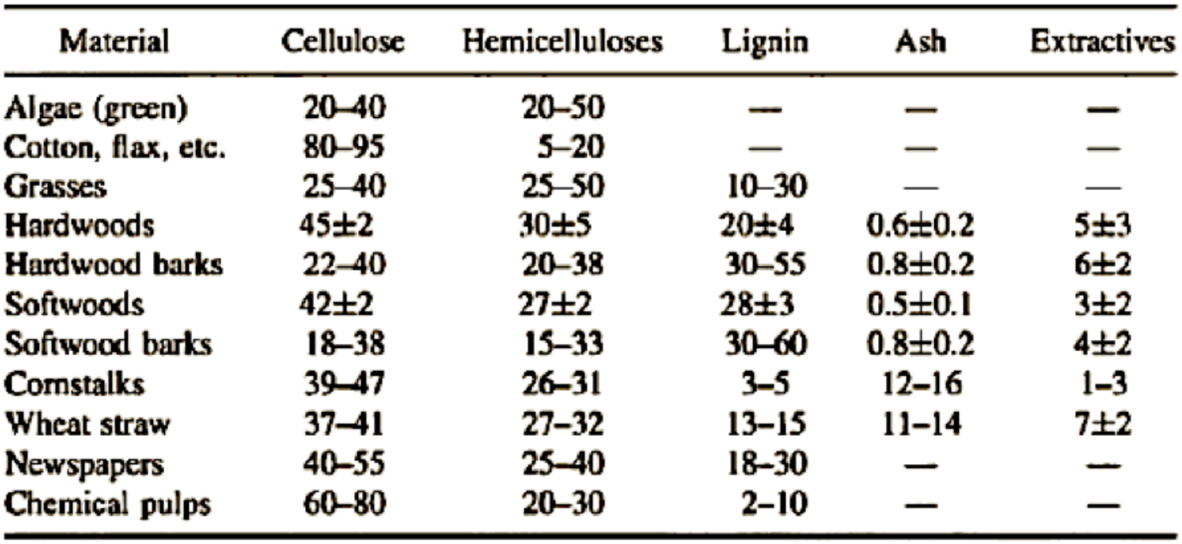
The recent focus on increased ethanol production has put the possibility of industrial level of butanol production in a shadow. Furthermore, the ability to gain high yields of ethanol from corn using yeast has created an incentive to produce ethanol over butanol, which suffers from low yields. Many states have amplified the effect of this shadow by promoting the production of ethanol which is done through tax credits, tax exemptions, federal and state loans, and grants to build and maintain ethanol producing facilities.

The use of biomass as an input into the creation of fuel is a step forward in the development of a more renewable fuel source, because the energy can be grown rather than fossil fuels being pumped from beneath the surface. Fossil fuels take millions of years to form, and thus are limited in supply. The amount of fossil fuel that still remains is largely debated, but the need for an alternative to ease the consumption of fossil fuels is a commonly accepted. An ideal solution would involve separating the food source from the energy source. A report done by Aleksic Snezana, a student at Youngstown State University, suggested that the amount of ethanol that it takes to fill a sport utility vehicle, around 100 liters, would have to be derived from enough food to sustain one human for a year, roughly 240 kilograms. (Butanol Production from Biomass, May 2009)

It is well understood that directly connecting the food and energy supply to the same source would create a delicate balance. A rise in the cost for a certain crop could result in the rise of fuel costs. Likewise, a high demand for fuel could cause a rise in the cost of food. Economist Dr. Bruce Babcock, (Iowa State University) analyzed this effect 2008. (Breaking the Link between Food and Biofuels, Bruce Babcock). In the report, Professor Babcock explained that the result of the use of any crop used for the production of biofuel would inadvertently effect production of food. If the United States increased it production of that crop that was being used to create biofuel, it would be at the cost of another crop. The allocation of land that is fit for agricultural harvesting is largely accounted for. This means that the U.S. has the ability to only produce so much food and increase in one causes a decrease in another.

Some forms of biomass can be used such as wood and waste paper but in many cases the fuel is more expensive to produce with smaller yields of product. There is also a substantial risk in producing large quantities of one crop because changes in weather patterns make it impossible to predict yield of crops. Two forms of feedstock are being considered for yeast and bacteria, lignocellulosic material and non-cellulosic material to produce butanol and ethanol. Lignocellulosic derived feedstock can be broken down into cellulose, hemi-cellulose, and lignin. The lignocellulosic material needs to be pretreated in order to break it down into simple monomers of glucose which can than be fed to the bacteria. Although plant matter that contains starch is normally food for humans, it is also very easy for enzymes to break it down into sugars, which makes it an easier source of feedstock for bacteria. For example corn, which is the current microbial feedstock for almost all industrial biofuel producers, is primarily comprised of starch. The table below shows some of the various types of cellulosic material that could be used as feedstock for bacteria, but would not create a connection between food supply and energy supply.

Table 2.2

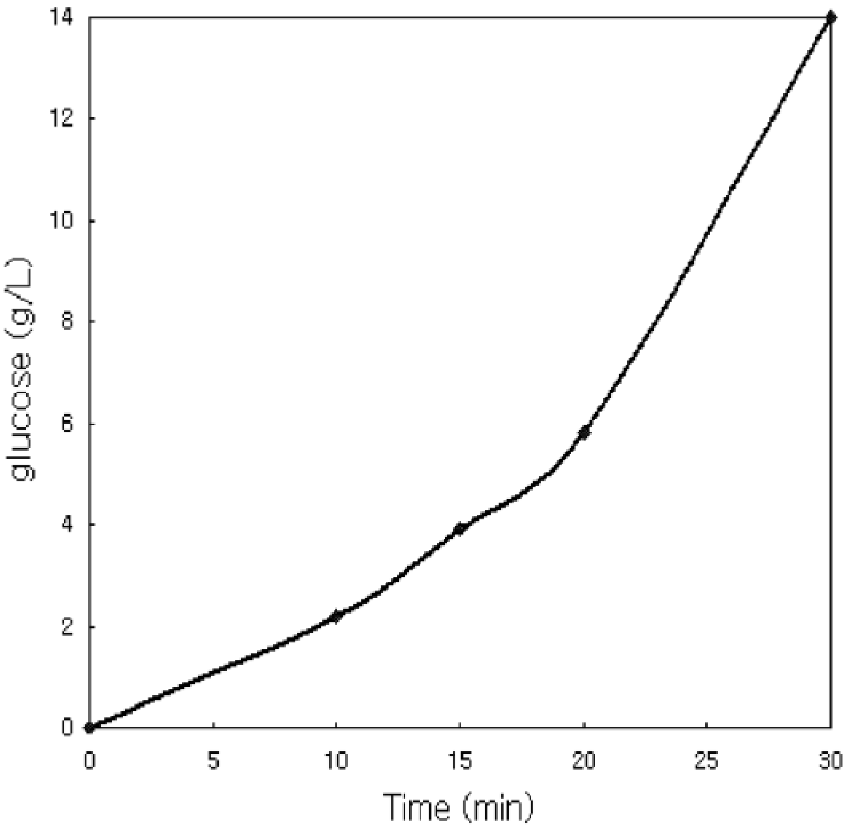


Material	Cellulose	Hemicelluloses	Lignin	Ash	Extractives
Algae (green)	20–40	20–50	—	—	—
Cotton, flax, etc.	80–95	5–20	—	—	—
Grasses	25–40	25–50	10–30	—	—
Hardwoods	45±2	30±5	20±4	0.6±0.2	5±3
Hardwood barks	22–40	20–38	30–55	0.8±0.2	6±2
Softwoods	42±2	27±2	28±3	0.5±0.1	3±2
Softwood barks	18–38	15–33	30–60	0.8±0.2	4±2
Cornstalks	39–47	26–31	3–5	12–16	1–3
Wheat straw	37–41	27–32	13–15	11–14	7±2
Newspapers	40–55	25–40	18–30	—	—
Chemical pulps	60–80	20–30	2–10	—	—

(Snezana Aleksic, 2009)

Picking the proper feedstock for use in a production facility has many different properties that get factored into the decision. Companies pick their cellulosic feedstock based on availability of the resource in the area, the costs associated with purchasing or harvesting, transportation costs, handling costs, and the possible outputs. Some companies and researchers have looked for feedstock from other sources than those listed above. For example, the Korea Ocean Research and Development Institute was given a patent on July 27, 2010 for what they believe is the most efficient feedstock. The title of the patent states*, “Liquefied extract if marine algae for producing bio-ethanol under high pressure and method for producing the same.”* Described in the patent is a process for the liquefying algae to use as a feedstock, and also a fermentation process. Marine algae are a readily abundant source of glucose, which grow in a variety of ways and locations in the ocean. In many places, algae is considered to be an environmental pollutant because of it tendency for overgrowth. This enhances its image as a possible media source because it grows quickly allowing for easy harvesting techniques. After collecting a sufficient amount, the algae are placed in a heated unit where pressure can be increase to a range of 500-1000 MPa. The process is left for approximately thirty minutes. The process is a very simple procedure, and most importantly inexpensive. The algae tissue degrades during this process, which leaves a resulting liquid that contains a portion of glucose. The liquid is then fed to bacteria strains, which in turn can produce butanol or ethanol. The graph below shows the extracted glucose from a 100-gram sample of *Ulva pertusa*.

FIGURE 2.2



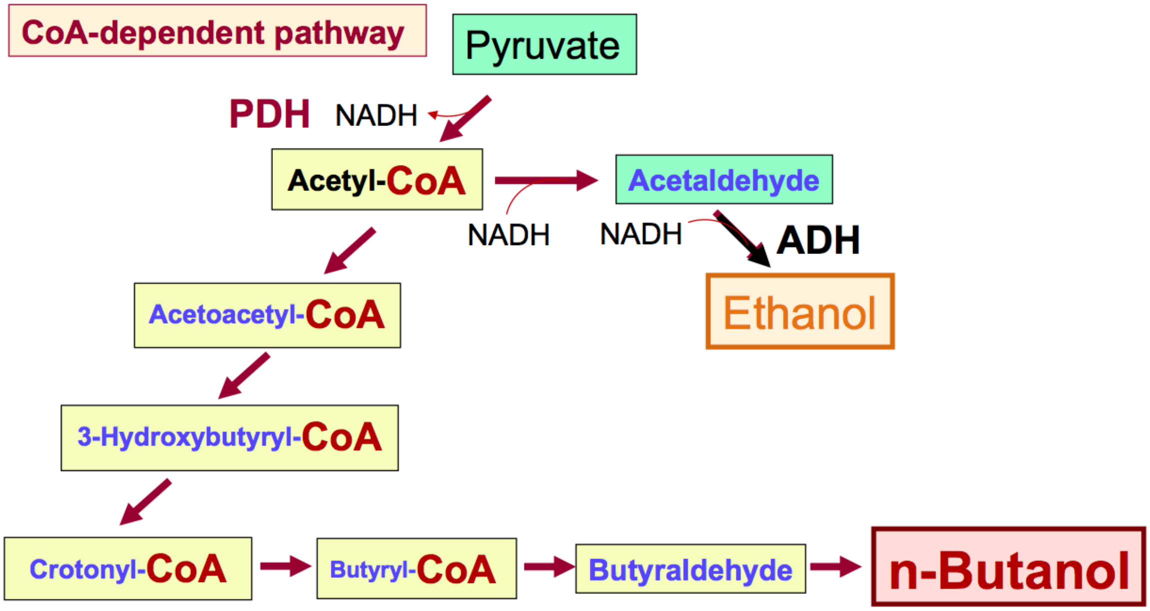
(the Korea Ocean Research and Development Institute, 2010)

The glucose that is collected from this process is used as feedstock for bacteria or yeast. The glucose is then be fermented using conventional methods of fermentation. The product that exits the bioreactor is then distilled into pure ethanol. The idea of using algae as a feedstock is an interesting concept because it alternative societal use is extremely limited and there is an abundant supply for harvesting. Algae are also a very diverse and located in most temperate climates of the world, which would help allow nations who have coastline to help sustain their energy consumption.

Although new methods of producing butanol and ethanol emerge as new technology and strains of bacteria develop, the production pathway remains a fairly standard procedure. Production normally uses bacteria for butanol, usually from the *Clostridium* family, and most commonly creates three parts acetone, six parts butanol, and one part ethanol. The microbes are placed in a sterilized bioreactor, insuring that the selected microbial source is the only microbe found in the reactor. Controls are needed to regulate environmental conditions for the bacteria to survive in the reactor. The bacteria will consume what is commonly referred to as either media or feedstock, and ultimately produce mixture of the desired product, and byproducts of the reaction. Ethanol, which is produced on a much larger scale than butanol, follows a fairly less extensive pathway to its production. Pretreatment processes for corn are simple and inexpensive, which means that feedstock for the bacterium is easy to produce. The yeasts used for industrial levels of production have been genetically engineered to produce high yields of product and withstand toxic levels of the alcohol that they produce. One of the main problems encountered by many scientist trying to produce high yields of biofuel through bacteria or yeast, is that the microorganism dies after the levels of alcohol become more and more toxic. This is seen more in butanol production rather than in ethanol production, but is a hindering factor in both processes. As new forms of bacteria and yeast are genetically engineered, patents are filed for the new strains.

Production of ethanol and butanol from microbes follow a fairly general production pathway, although the pathway to production of butanol is more extensive than the pathway to ethanol. The diagram below shows the two pathways for Ethanol and Butanol, starting with pyruvate, which is a product of glucosysis (from a glucose source) or the Pentose Phosphate Pathway (from a pentose source). Enzymes, or biocatalysts, facilitate chemical reactions that breakdown glucose into pyruvate. Different enzymes are able to direct different reactions, which aid in the various stages of the production pathway. Each different strain of bacteria or yeast has unique characteristics that impact their productivity at following the pathway.

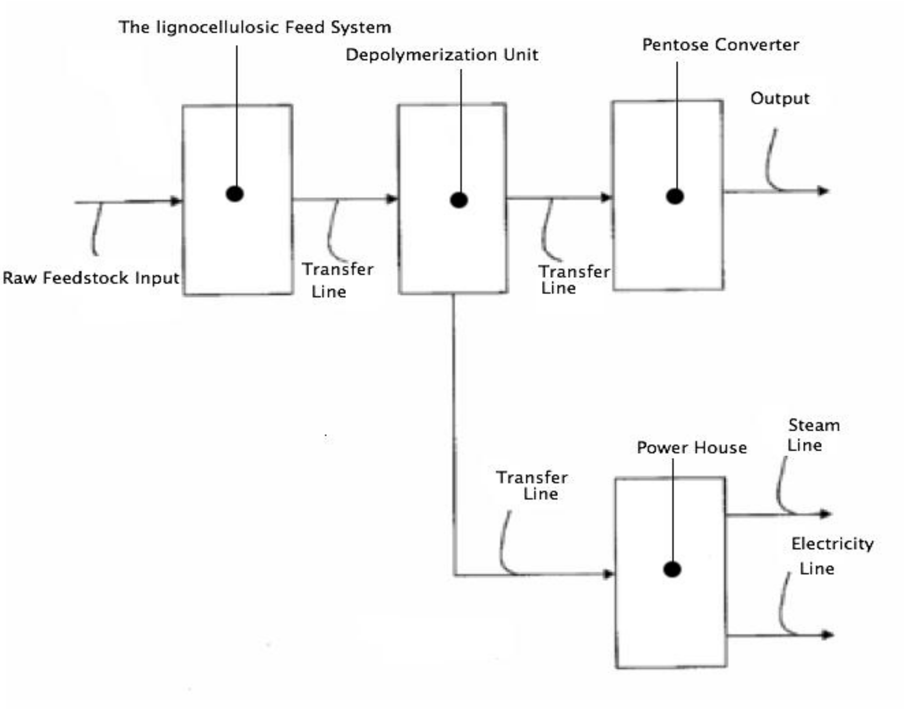
FIGURE 2.3



(James C Liao, 2006)

Although the production pathway is fairly standard, there are a wide range of processing techniques which are specific to every company. As these individual companies do research on their own processing techniques and create new techniques, they patent their finding. On June 17, 2010, the United States Patent and Trademark Office published an application that was submitted by British Petroleum. The application is entitled “Process, Plant and Butanol from Lignocellulosic Feedstock” (app #20100152496) encompasses a process designing a manufacturing plant for the production of lignocellulosic material. The patent, gives a extensive description of the processes which lead to the final product, a slurry mix which contains enough glucose to be fermented. The application mentions in the claim section some notable forms of feedstock that would be compatible in the process as corn maize, wood, paper waste, and agricultural waste. In this specific application, a depolymerization step is used to separate the cellulose from the hemi-cellulose, because the process uses the two feedstocks separately. The segregation of pentose and glucose works to allow specialized species of bacteria to consume pentose and another specialized species for glucose. Pentose is then derived from the hemi-cellulose, and refers to the cellulose as a, “remainder.” This remainder can be handled in the described process in two ways. It can be burned in order to create energy from heat, or it can be converted further into biofuel from another microbial culture. The patent is accompanied by some illustrations to assist the readers understanding of the process and is provided on the following page.

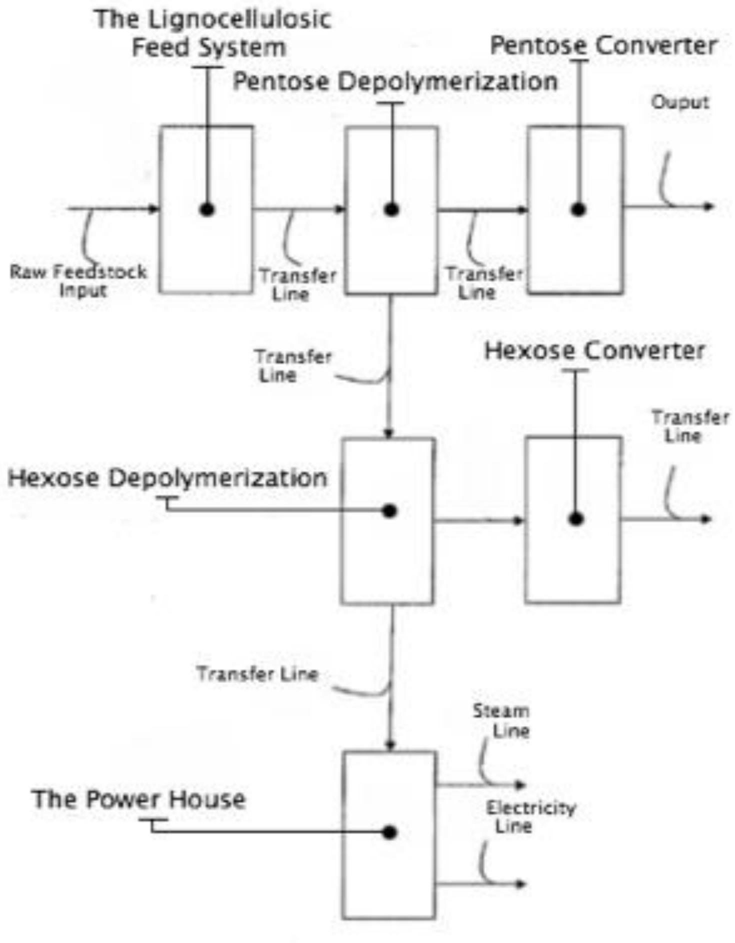
FIGURE 2.4



(British Petroleum, 2010)

Figure 2.5 is a process design that represents the processing plant which pre-treats lignocellulosic material so that it can be used during a fermentation process. The first arrow into the system (top left of the schematic represents an input of raw feedstock that could be a conveyer belt, pipeline, or any other device for transporting lignocellulosic feedstock into what the patent named, “The lignocellulosic feed system.” The feed system pre-treats the raw feedstock which can include cutting, chopping, heating, or any other preference of the system the depolymerization unit might require. The pretreated feedstock would be transported to a depolymerization unit, where depolymerization would begin. Depolymerization separates the pentose and a remainder. The pentose exits the depolymerization and is put into, “a pentose converter,” unit via a transfer line. The pentose converter is a bioreactor, where a microbe ferments the treated feedstock into butanol or ethanol. The ethanol or butanol would exit this stage production and be stored accordingly. The patent gives two possible options for dealing with the remainder (mostly comprised of cellulose and lignin) created from pentose. In the powerhouse method, shown in figure 2.5, remaining material from pentose depolymerization is used to create steam or electricity by burning it. The electricity that is created can be used to help power some of the processes which have been described, or steam can be used to assist in the feed system. Another option for dealing with the remainder is shown in figure 2.5.

FIGURE 2.5

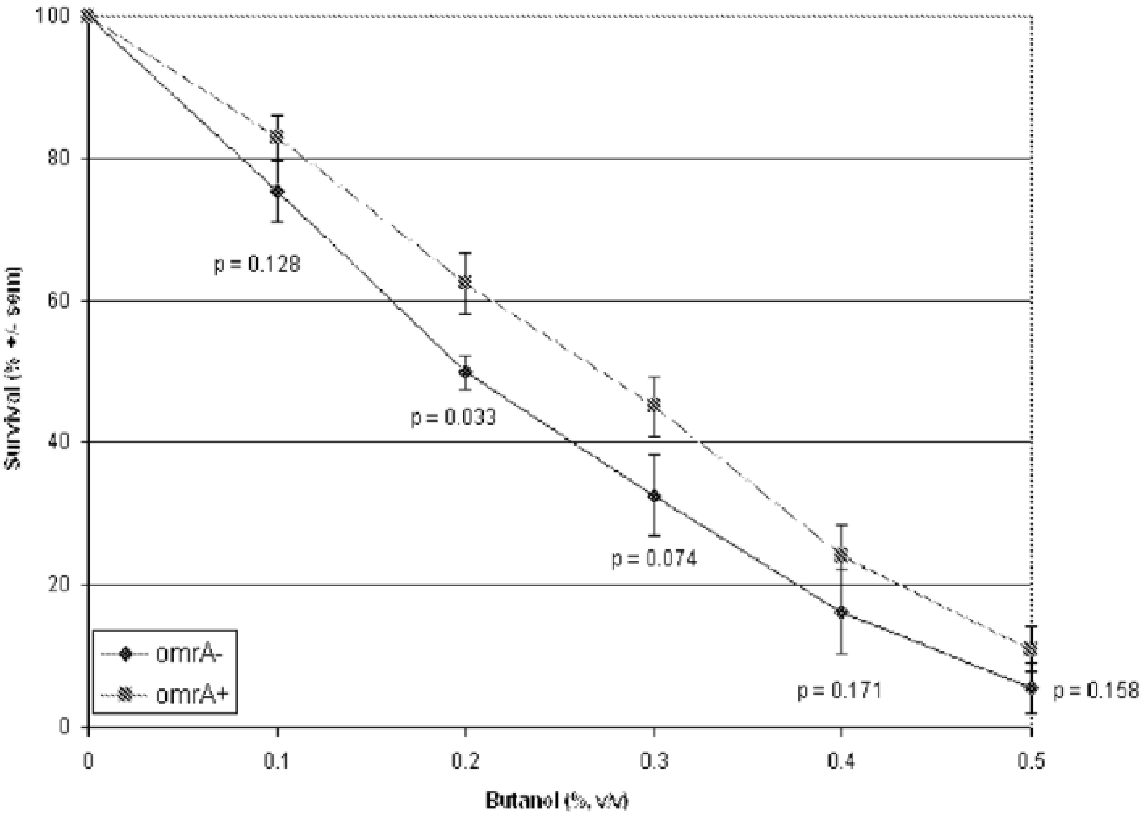


(British Petroleum, 2010)

Figure 2.5 represents a processing plant much like figure 2.4 but instead of sending the remaining cellulose and lignin into a powerhouse, it undergoes a process to convert it into butanol or ethanol. The pentose proceeds to follow the same process that was exemplified in figure 2.5, although the path of the remaining feedstock is altered to first pass through a hexose depolymerization unit. The hexose depolymerization unit uses different enzymes or another processing treatment to produce hexose and a second remainder. This refined remainder is then sent to a powerhouse that continues the same process to produce steam and/ or electricity. The hexose that is produced is then transferred into a hexose conversion unit, more commonly known as a bioreactor. The difference between the hexose conversion unit and the pentose conversion unit is simply a different microbial culture that is more efficient at consuming hexose. Although the designs are not specific in detail about each step, the schematic shows how a plant would likely produce ethanol or butanol at industrial standards.

Innovations described so far have regarded processing plant designs and methods of producing butanol, although innovation regarding enhanced facilities or different inputs regarding production of butanol or ethanol. Enhancing the genetics of the microbial sources that ferment the media is another area of innovation. Bacteria do not have the ability to grow once certain concentrations of alcohol have been reached within the bioreactor, because butanol is toxic to bacteria at relatively low levels. This has pushed researchers to mutate bacteria to help enable bacteria to reduce the effect that butanol toxicity has on their growth. Most bacteria find butanol toxic at 13 grams per liter (levels that are not commercially viable). Increasing the ability resistance of bacteria to this toxicity would make production facilities more economically viable. Integrated Genomics, a company that deals with genetic mutations in bacteria, was approved a patent on February 9, 2010, for a strain of bacteria that produces more efficient titers of butanol than industry standards. The cell is able to withstand higher intracellular and extracellular levels of butanol, than the original strain of *Clostridium Acetobutylicum*. The patent describes some genetic differences between wild strains of *Clostridium* and the strain that is patented, but the most notable one is an adapted, “multi-drug resistant,” protein. The patent claims that microbial cells expressing the MDR pump can tolerate higher levels of butanol as compared with a strain that is no expressing the MDR pump.

(**Figure 2.6**)



(Integrated Genomics, 2010)

The dotted line represents the survivability with the MDR pump, while the solid line with diamonds represents the survivability of microbial strain without the adaptation. The test results revealed that in almost all circumstances, the microbial source was better suited to survive butanol toxicity when its nucleic acid contained the OmrA protein. These gains were more noticeable a 20-30% butanol content by weight. Lab test also confirmed that strains of *Clostridium acetobutylicum* that over-expressed the Omra gene were on average, able to produce 39% more butanol than the strains that had not.

The interest levels in both ethanol and butanol as an alternative energy source have increased with many respects over the last ten years. Research and development on both alcohols has increased dramatically and many companies are continuing to look for more efficient methods for industrial levels of production. The levels of production in ethanol and butanol have also increased representing this growing interest. Both ethanol and butanol have a large potential to assist the growing energy usage in the United States, it seems as though ethanol has taken the spotlight over butanol and other sustainable fuels. The lower level of interest given to these possibilities has slowed their development dramatically. Comparatively analyzing butanol with gasoline yields similarities in many of the categories. Should the same analysis be done with ethanol, the results would show some significant differences. Despite these differences, ethanol is produced in much larger qualities because of it ease in production. It is likely that butanol production levels will build after production of ethanol leaves its innovative state, creating a more equal distribution of the focus from the energy sector.

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Chapter 3 Hydrogen

As fossil fuels and natural gas start to dwindle, even more people are looking to move away from a hydrocarbon economy and move towards hydrogen for their energy needs. This is because fossil fuels and natural gases are unsustainable and are a main cause of pollution, such as carbon dioxide. Hydrogen is looking to solve these problems. As the world's supply of hydrocarbons decreases, the demand for them increases. Advocates of hydrogen claim that hydrogen can be used as a cleaner alternative to fossil fuels and decrease their demand [Muller, 2003]. The term "hydrogen economy," which refers to the use of hydrogen as the main energy source, was first coined by John Bockris at a General Motors center in 1970. Since the 1970's, hydrogen lobbyists have been promoting the use of hydrogen as a fuel that can be used in motors such as cars and boats, for the energy needs of houses and buildings, as well as an energy source for handheld electronic devises [Pellerin, 2008]. The Hydrogen Economy is looking to solve the problems of today's energy.

Figure 3.1
Elements of the Hydrogen Economy
(World Meteorological Organization, 2009)

Hydrogen is listed in the periodic table with the chemical symbol H and the atomic number 1. Hydrogen is the lightest and most abundant element in the universe making up nearly 75% [University of California, 2003]. Hydrogen is the main component of Jupiter and other gas planets. The interior of Jupiter has a pressure so great that molecular hydrogen can convert into solid metallic hydrogen. Unfortunately pure elemental hydrogen is rarely found on earth naturally. Most of the Hydrogen can be found in chemical compounds such as water and organic compounds. However hydrogen can be produced in a number of ways. Currently steam reforming is the most common way to produce hydrogen. Most of the hydrogen gas generated today goes to the production of petroleum and is combined with nitrogen to make ammonia. The ammonia is used to make chemicals such as cleaning solutions and fertilizer. The United States alone makes millions of tons of fertilizer every year [Saarela, 1998]. However, the hope is that in the future hydrogen will be produced purely as a fuel.

Hydrogen is not an energy source but an energy carrier and can be a good resource for fuel cells and batteries. Many companies are trying to develop new technologies to exploit hydrogen for its full potential. There are many methods of producing hydrogen that are being used today. Steam reforming (figure 3.2) is a method of generating hydrogen with the use of methane or natural gas at high temperatures. At these high temperatures steam reacts with the methane or natural gas to create a synthetic gas. In the next step hydrogen is generated through a water gas shift reaction [US department of Energy, 2008]. The carbon monoxide compound strips the oxygen away from the water leaving hydrogen, but also producing carbon dioxide which is a pollutant. It is possible to capture the CO_2 and dispose of it by injecting it into an oil or gas reservoir. However, most industries simply choose to release it in to the atmosphere which is considered a major part of global warming [Brain, 2002].

Figure 3.2: Steam Reforming Reaction

(Brian, Marshall)

$CO + H_2O \rightarrow CO_2 + H_2$ - 40.4 kJ/mol.

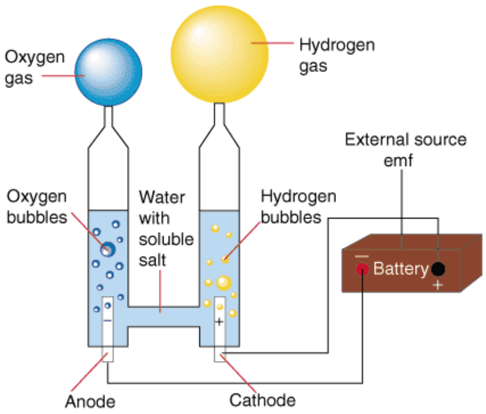


Figure 3.3: Simple Electrolysis Machine
(John R, 2010)

Electrolysis (Figure 3.3) is the splitting of water molecules by putting an electric current through it. This process creates both oxygen gas and hydrogen gas. Electrolysis is not the method of choice for hydrogen production but it is the easiest. This method produces hydrogen when an electric current passes through the water and the molecules split up; the oxygen goes toward the anode and the hydrogen goes towards the cathode (Figure 3.4). On the industrial level, production relies on high pressure and temperature to turn out a better yield. The drawback with the use of electrolysis is that it requires a large amount of energy to split the water. It is cheaper and more efficient to simply use fossil fuels to create hydrogen [Smith, 2008].

Figure 3.4: Electrolysis Reaction

(Smith, Constance)

energy + $2H_2O \rightarrow O_2 + 2H_2$

Thermo chemical water splitting is a relatively new way to produce hydrogen by using high heat (500-2000°C) to drive chemical reactions that only consume water and only produces hydrogen and oxygen. This is being considered for the Hydrogen Economy because production of greenhouse gasses is minimal during this process. This is because heat required for this method is generated by either solar or nuclear energy which are much greener ways of producing energy [US Department of Energy, 2008].

Microbes such as algae have been known to produce hydrogen under certain conditions [Bolt, 2009]. In 2000, it was discovered that a strain of algae, known as *Chlamydomonas reinhardtii* (Figure 3.5)*, when deprived of sulfur will produce hydrogen during their photosynthesis instead of oxygen [*Jaffe, 2006*]. Since then researchers have been looking to bioengineer algae and other forms of bacteria to produce hydrogen through their natural metabolic system. In 2008, researchers studied the solar to energy efficiency in Chlamydomonas reinhardtii* mutants and found that they had 25% efficiency which is considered exceptionally high [Melis, 2008]. Current research is being focused on microbes that have the ability to produce sufficient amounts of hydrogen.

Figure 3.5: *Chlamydomonas reinhardtii*

(Cody Cobb. 2009)

Hydrogen Production is one of the main problems facing the outlook of the use of hydrogen as a fuel. The current way of using fossil fuels to create hydrogen produces greenhouse gasses and is not sustainable for future use. This is why research is being done to develop a new cleaner way to create hydrogen. Microorganisms are being looked at as a way to accomplish this. Anaerobic microbial cells that have the ability to produce hydrogen in an amount that could be industrially useful can be a big help to our hydrogen needs. Biological production of hydrogen is a much cleaner method than steam reforming because it produces no CO. The use of hydrogen producing microbial could be a way to create a cleaner energy source [Yukawa, Hideaki, Noriyuki Yamamoto, 2008].

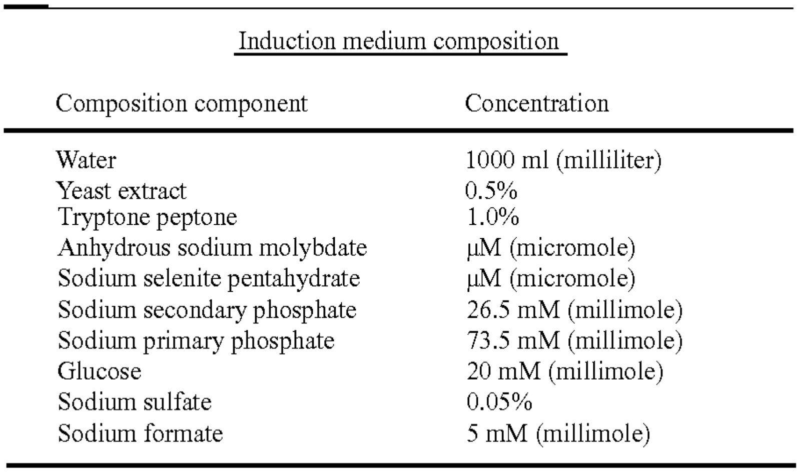
The problem with the use of microorganisms to produce hydrogen today is that the methods are relying on the division and proliferation of anaerobic microorganisms. That is, a method couldn’t be found to obtain a high density anaerobe that could create hydrogen in a short time. The invention being reviewed aims to solve the problems regarding hydrogen production using anaerobic microorganisms (Yukawa, Hideaki, Noriyuki Yamamoto, 2008).

This invention aspires to obtain anaerobic microbial cells in an amount large enough that, within a short time, can produce an industrially beneficial amount of hydrogen. This is said to be accomplished by culturing a microorganism having a formate dehydrogenase gene and a hydrogenase gene under aerobic conditions in a liquid medium containing formic acid and then using the cells made to produce hydrogen. Hydrogen made by this method can be used as fuel for fuels cells or the like (Yukawa, Hideaki, Noriyuki Yamamoto, 2008).

This invention consists of three steps. The first step is culturing particular microbial cell under aerobic conditions to proliferate and divide microbial cells. The objective of this step is to produce enough microbial for making hydrogen. Microbial don't produce hydrogen after being produced under aerobic conditions. Because of the ethanol, lactic acid, and acetic acid are formed during the process as well and slow the process down during the third stage, one must remove the bacteria from the culture. The second step regards the microbial gaining the ability to produce hydrogen. Once the microbial is introduced to a formic acid culture under anaerobic conditions, they have the ability for hydrogen generation. The third step concerns the addition of microbial cells that have the ability to generate hydrogen and the addition of an organic substrate [Yukawa, Hideaki, Noriyuki Yamamoto, 2008].

Specific microorganisms that could be used in this invention are in the genus *Escherichia*, *Klebsiella*, *Enterobacter*, or *Clostridium*. For the first culture, it is performed using a nutrient medium that consists of a carbon source, a nitrogen source and an inorganic source. Culture conditions with respect to temperature and pH range between 20 to 40°C and 6-8 respectively. This pH is maintained by a phosphate buffer of about 6.5. Under these conditions the growth is optimal within eight hours but the cells are unable

Table 3.1
(Yukawa, Hideaki, Noriyuki Yamamoto).



Induction medium composition

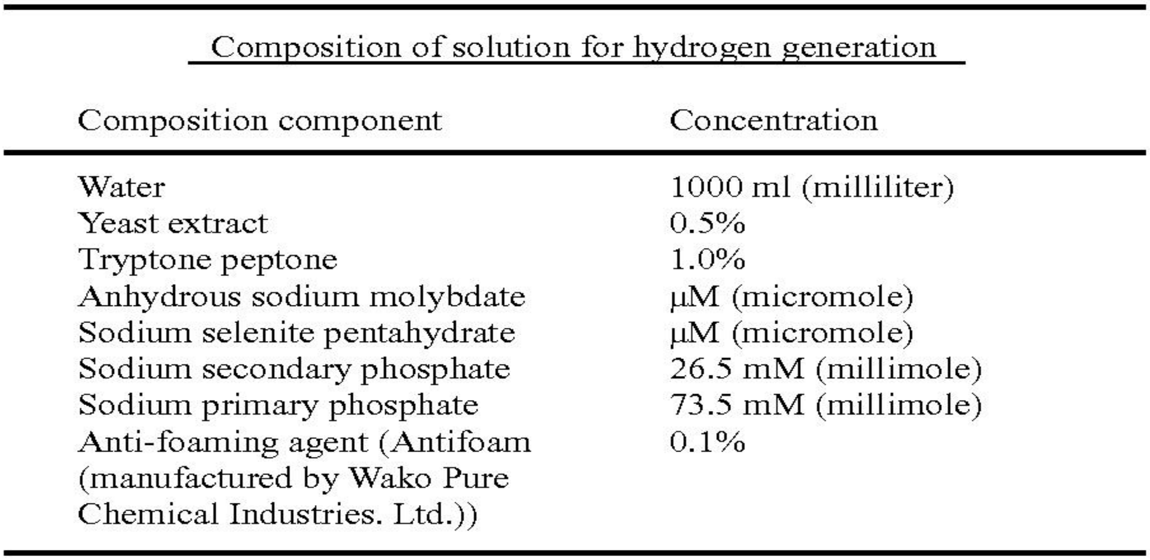
Composition component	Concentration
Water	1000 ml (milliliter)
Yeast extract	0.5%
Tryptone peptone	1.0%
Anhydrous sodium molybdate	μM (micromole)
Sodium selenite pentahydrate	μM (micromole)
Sodium secondary phosphate	26.5 mM (millimole)
Sodium primary phosphate	73.5 mM (millimole)
Glucose	20 mM (millimole)
Sodium sulfate	0.05%
Sodium formate	5 mM (millimole)

to produce hydrogen (Yukawa, Hideaki, Noriyuki Yamamoto, 2008).

The second step requires the removal of the microbial cells from the first culture and being added to a second culture containing formic acid. The composition of the medium of formic acid (Table 3.1) should satisfy the conditions under which the microbial cells can divide at least once. For this to happen, a carbon source in medium should be used. Sugars such as glucose are commonly used as the carbon source. Enzymes that are involved in the pathway of forming hydrogen from formic acid are hydrogenase and formate dehydrogenase. These enzymes are present in the membrane of the microbial cell and function as a unit pair. Formic acid helps in the expressing of these genes which allows the microbial to produce hydrogen [Yukawa, Hideaki, Noriyuki Yamamoto, 2008].

A third step involves the recovery of the hydrogen producing cells and adding them to a solution for hydrogen generation (Table 3.2) and an organic substrate is added continuously to produce large amounts of hydrogen. This solution has generally the same composition as the medium used in the second step. However, this hydrogen generation is more aggressive, and therefore it is recommended to use an anti-foaming agent; for example, a silicon or polymer based antifoaming agent which are both commercially available (Yukawa, Hideaki, Noriyuki Yamamoto, 2008).

Table 3.2: ((Yukawa, Hideaki, Noriyuki Yamamoto).



Composition of solution for hydrogen generation

Composition component	Concentration
Water	1000 ml (milliliter)
Yeast extract	0.5%
Tryptone peptone	1.0%
Anhydrous sodium molybdate	μM (micromole)
Sodium selenite pentahydrate	μM (micromole)
Sodium secondary phosphate	26.5 mM (millimole)
Sodium primary phosphate	73.5 mM (millimole)
Anti-foaming agent (Antifoam (manufactured by Wako Pure Chemical Industries. Ltd.))	0.1%

According to the method of this invention, an extremely high hydrogen generation rate, and a quick response to a supply of organic substrate can be achieved. This technique could also be an exceptional plan for supplying hydrogen fuel for fuel cells [Yukawa, Noriyuki, 2008].

Anaerobic digestion provides a potentially improved way of producing hydrogen as compared to the use of hydrocarbons. The production of hydrogen by bacteria is inexpensive and can be done with reusable energy sources such as organic waste. Many studies have shown certain strains of bacteria produce large quantities of hydrogen as a by-product of their natural anaerobic digestion of organic waste. This is why bacteria are being looked at as a solution to creating hydrogen (Hansen; Dae-Yeol, 2009).

There is one problem with using anaerobic digestion of organic waste to create hydrogen. That is, when using organic waste such as manure to feed bacteria, other naturally occurring bacteria will be present in the organic matter. Many of these bacteria consume hydrogen. Therefore with non-sterile substrate will consist of hydrogen producing and hydrogen consuming bacteria. With this the hydrogen consuming bacteria will grow until nearly all of the hydrogen produced is subsequently consumed (Hansen; Dae-Yeol, 2009).

Systems have been developed to allow hydrogen production in an anaerobic digester but these systems typically require keeping the strains of hydrogen bacteria pure and sterilizing the organic matter used. The problem with these systems is that they are not commercially feasible. This is because keeping the bacteria pure is very difficult and sterilizing all the organic matter is very expensive. There is another method that uses heat treatment to kill all the hydrogen consuming bacteria while the hydrogen producing bacteria live by making spores but this method is also very expensive. The present invention aims to create a system for the production of hydrogen from anaerobically digesting organic waste that is cost effective and more efficient (Hansen; Dae-Yeol, 2009).

The mission of this invention is to effectively produce hydrogen by anaerobic digestion by having bio-mass containing hydrogen producing bacteria or spores that is treated with a chemical agent in one aspect. In the other aspect, having the biomass used in a bioreactor to aerobically digest a non-sterile organic substrate to produce hydrogen. The bio- mass is created in a mixed culture containing both types of bacteria, at least one type of hydrogen producing bacteria and at least on type of competing bacteria, and a chemical agent that subsequently kills all the competing bacteria while not hurting the hydrogen producing bacteria. Because the organic matter is non-sterile, it has more than just hydrogen producing bacteria on it. The enriched biomass is combined with the organic matter so that the hydrogen producing bacteria overcome the competing bacteria on the organic substrate so they can consume the organic matter and produce hydrogen. The chemical treatment includes one or more of pH treatment, antibiotic treatment, methanogenic inhibitor treatment, similar chemical treatments, and any combinations of these (Hansen; Dae-Yeol, 2009).

The biomass is produced using a mixed culture of anaerobic bacteria. Mixed cultures with hydrogen producing bacteria and competing bacteria occur naturally. There can be any number of hydrogen producing bacteria. Some common species of hydrogen producing bacteria can be found in the genus *Clostridium*. They are gram-positive, spore forming rods that are anaerobic. Hydrogen producing bacteria don't need to be picked specifically when using non-sterile biomass because they occur naturally. Using non-sterile material over sterile is advantageous because it is very expensive to keep the material in sterile conditions (Hansen; Dae-Yeol, 2009).

A chemical agent is selected to produce a bacterial stress response or an inhibitory effect on bacteria in the biomass. The chemical agent is used to either produce more hydrogen producing bacteria or decrease the number of competing bacteria in the biomass. Suitable chemical agents include acids, antibiotics, or methanogen inhibitors. Good acids to use are perchloric acid, sulfuric acid, phosphoric acid, hydrochloric acid, or nitric acid. The acid is usually selected according to cost. An example of a good methanogen inhibitor is sodium 2-bromoethanesulfonate and an example of an antibiotic is rumensin. The Chemical treatment produces an enriched biomass (Hansen; Dae-Yeol, 2009).

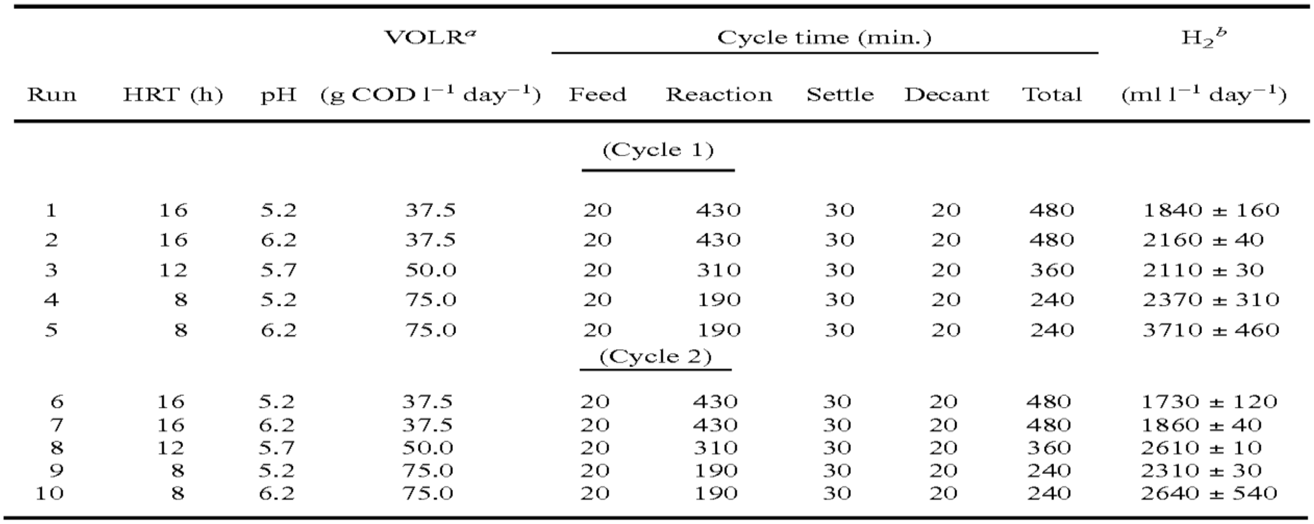
As long as the treatment does not kill the bacteria, any number of chemical treatments can be used on the biomass for however long you want. There is a sliding scale to the harshness and duration of the chemical treatment. The harsher the chemical used, the less time it should be applied. The inventors of this invention have found that the enriched biomass can be formed without heat treating by lowering the pH of the biomass substantially below 3.7.   At this pH, the acid content becomes sufficient in killing the hydrogen consuming bacteria and lowers the need for heat (Hansen; Dae-Yeol, 2009).

There are many examples on how to do this in a way that produces a good amount of hydrogen that can be useful for fuel. These are experiments carried out by the inventor and one of these methods is examined below. This is not the only way to carry out this process.

Sludge was taken from the bottom of an induced blanket reactor at a cattle manure wastewater treatment plant. The sludge was kept at 3 pH and 35°C and held for a period between 24 and 72 hours. It possessed characteristics of Clostridia, a hydrogen forming bacteria. The sludge then went through another treatment so that the Clostridia could form spores. The substance was then treated with perchloric acid to reduce the pH to 2.0. These spores helped enrich the biomass. This biomass was then digested with a non-sterile substrate in a semi-continuous anaerobic sequencing batch digester. The ratio of enriched biomass to organic substrate was about 1:9. This biomass was digested in two parts. During part one (Table 3.3) the hydraulic retention time was varied between 8 and 16 hours and during part two (Table 3.4) the hydraulic retention times were varied between about 4 and 12 hours. These steps were conducted at a pH of 5.2-6.2 (Hansen; Dae-Yeol, 2009).

Table 3.3: Hydrogen Production during Part1

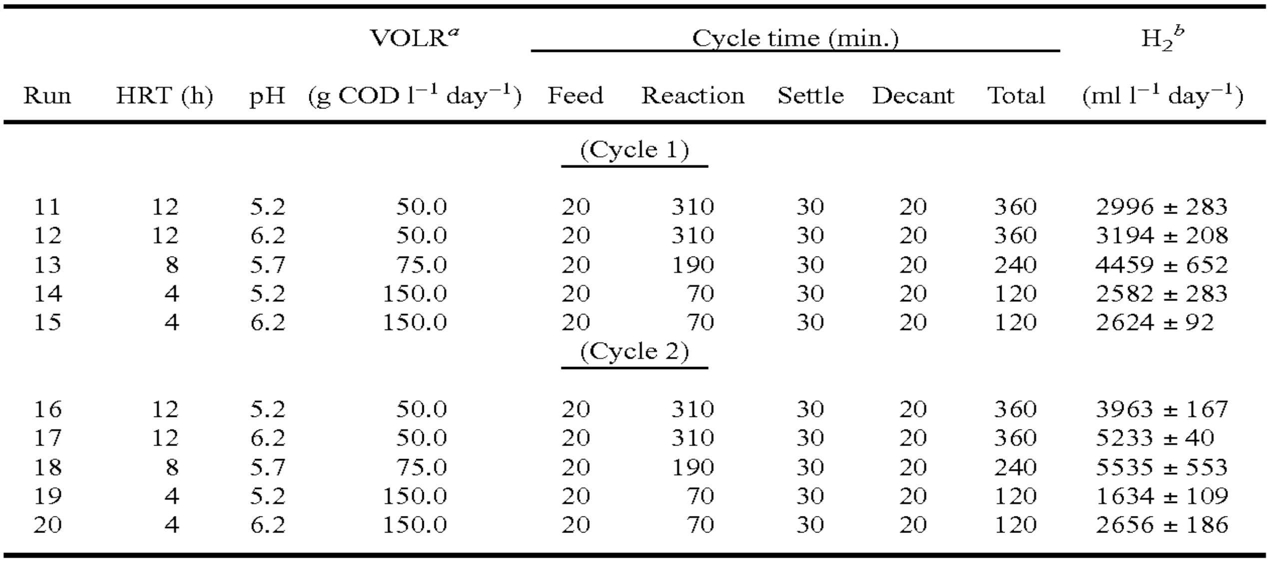
(Hansen, Conly)



			VOLR[a]	Cycle time (min.)					H_2[b]
Run	HRT (h)	pH	(g COD l^{-1} day^{-1})	Feed	Reaction	Settle	Decant	Total	(ml l^{-1} day^{-1})
				(Cycle 1)					
1	16	5.2	37.5	20	430	30	20	480	1840 ± 160
2	16	6.2	37.5	20	430	30	20	480	2160 ± 40
3	12	5.7	50.0	20	310	30	20	360	2110 ± 30
4	8	5.2	75.0	20	190	30	20	240	2370 ± 310
5	8	6.2	75.0	20	190	30	20	240	3710 ± 460
				(Cycle 2)					
6	16	5.2	37.5	20	430	30	20	480	1730 ± 120
7	16	6.2	37.5	20	430	30	20	480	1860 ± 40
8	12	5.7	50.0	20	310	30	20	360	2610 ± 10
9	8	5.2	75.0	20	190	30	20	240	2310 ± 30
10	8	6.2	75.0	20	190	30	20	240	2640 ± 540

Table 3.4: Hydrogen production during Part 2

(Hansen, Conly)



			VOLR[a]	Cycle time (min.)					H_2[b]
Run	HRT (h)	pH	(g COD l^{-1} day^{-1})	Feed	Reaction	Settle	Decant	Total	(ml l^{-1} day^{-1})
					(Cycle 1)				
11	12	5.2	50.0	20	310	30	20	360	2996 ± 283
12	12	6.2	50.0	20	310	30	20	360	3194 ± 208
13	8	5.7	75.0	20	190	30	20	240	4459 ± 652
14	4	5.2	150.0	20	70	30	20	120	2582 ± 283
15	4	6.2	150.0	20	70	30	20	120	2624 ± 92
					(Cycle 2)				
16	12	5.2	50.0	20	310	30	20	360	3963 ± 167
17	12	6.2	50.0	20	310	30	20	360	5233 ± 40
18	8	5.7	75.0	20	190	30	20	240	5535 ± 553
19	4	5.2	150.0	20	70	30	20	120	1634 ± 109
20	4	6.2	150.0	20	70	30	20	120	2656 ± 186

The total gas concentration of this procedure depended on the hydraulic retention time. The hydrogen content in the total gas produced decreased to a low value of 13-25% at the hydraulic retention time of 4 h, compared to 30%-57% at the hydraulic retention time of 8, 12 and 16 h. The optimum conditions for hydrogen production were found to be a retention time of 8 hours and a pH of 5.7. The yield for these conditions was 4460-5540 ml/day with a hydrogen composition of 43%-57% with no methane. These were the optimal conditions but all runs produced a significant increase in hydrogen production (Hansen; Dae-Yeol, 2009).

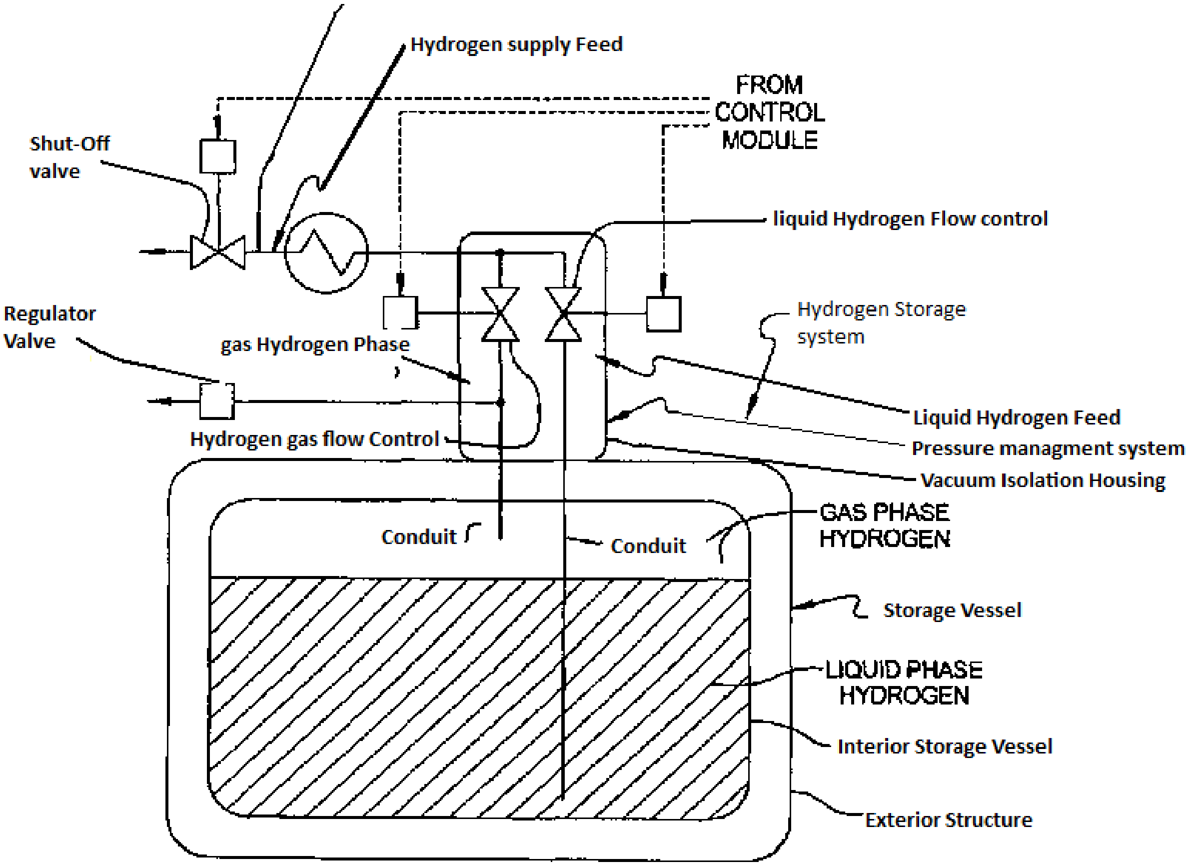
These inventions are looking for a better, cheaper way of producing hydrogen. The use of bacteria looks to be a good way of doing this. Using hydrocarbons to produce hydrogen is not sustainable and creates harmful pollutants that are considered responsible for global warming. Bacteria produce hydrogen naturally through their metabolic system then the hydrogen can be used as fuel. Microorganisms could be the answer to all the energy needs of the future but more research needs to be done.

Hydrogen storage is one of the main issues that stand in the way of the hydrogen economy. Methods under consideration for storage include high pressure, cryogenics, liquid hydrogen, and the use of chemical compounds. Liquid hydrogen is only viable in space shuttles because it takes a large amount of energy to cool it down to liquid state (about 20 K). Compressed hydrogen tanks are usually made out of aluminum or steel but are very big and bulky which make them difficult to put on motor vehicles. There is also a safety issue with these tanks and leaking is an ongoing concern. Another option is ammonia; it provides very high hydrogen storage densities and can be stored either as a liquid or in solid form which makes it a good alternative. A novel storage type is the use of metal hydrides. At high temperatures and at the right pressure, these hydrides can absorb large quantities of hydrogen. With these it is possible to store a large amount of hydrogen in a smaller space. Hydride is much more stable than hydrogen by itself and is considered safe in a catastrophic event such as a car collision. This is because hydride needs to be heated to release the hydrogen but in a crash the tank would break which would cool the hydride stopping the hydrogen release. Research is still ongoing on all of these possible solutions (Saarela, Emily).

Hydrogen storage systems have been setup to feed hydrogen into fuel cells and internal combustion engines. The hydrogen is usually stored in a vessel in either a gas or a liquid state stored at low temperatures and at high pressure. The problem with this is that when the pressure is too high, a large amount of the hydrogen is lost and vented into the surroundings. US7,690,208 *Liquid hydrogen tank with a release pressure above the critical pressure* by Rainer Immel provides a pressure management system that regulates hydrogen gas release from the storage tank when the pressure exceeds the maximum threshold. The hydrogen storage system (Figure 3.6) includes a storage vessel, an interior vessel structure vacuum, within an exterior vessel. The hydrogen is stored within the vessel under pressure. Special tanks have been designed to keep the hydrogen at around 20-30 K. At this temperature the hydrogen is in two distinct phases. The pressure of the vessel depends on the partial pressures of the liquid phase hydrogen and the gas phase hydrogen. If heat in some way enters the vessel some of the liquid hydrogen converts to a gas and the overall pressure of the vessel increases. The pressure management system regulates the pressure inside the vessel. This system includes a hydrogen supply feed, a hydrogen gas feed, and a hydrogen liquid phase feed encased in the vessel. There is also a regulator valve connected to the gas phase feed and is in constant communication with it. The regulator valve prevents the hydrogen tank from surpassing the pressure threshold. The regulator

Figure 3.6: Hydrogen Storage System

(Immel, Rainer)



valve is used to vent gaseous hydrogen into the surroundings with the pressure in the tank becomes too much. This way the pressure of the system is maintained (Immel, 2010).

A liquid hydrogen tank with a boil off pressure above the critical point has shown many advantages over tanks with boil off pressure below the critical point. The main advantage is that the hydrogen loss from the critical tanks is much less than the conventional tanks. In a long term boil-off test done by the inventor, the 3.0 MPa super critical tanks always had more hydrogen than the 0.8 MPa conventional tanks. The super critical tank was also tested in the amount of distance a vehicle could travel with zero lost. The super critical tank traveled 60 kilometers a day with zero loss of hydrogen which is not possible with a conventional tank. The critical tank also has a higher density capacity (Immel, 2010).

The hydrogen tank with a boil-off point above the critical point also has advantages over cryogenic tanks. This is because the critical tanks have less weight than the cryogenic tanks. The low weight id due to the design pressure per vessel is less, reducing the wall thickness. Weight is very important for automobile applications. Also the critical tanks have a zero refueling loss. This is because both the thermal mass of the super critical inner tank and the heat capacity of the remaining warm gas are much smaller than those of the high pressure cryogenic vessel (Immel, 2010).

Fuel cell systems have increasingly become a power source for many applications but having an efficient way of storing the hydrogen for the fuel cells is very important (more information in Chapter 4). In addition, it is important that these tanks don't lose hydrogen. This is why it is important to have a pressure management system to help reduce hydrogen loss like the one reviewed (Immel, 2010).

Metal hydrides are elements, alloys, or intermetallic compounds that have the chemical property of reversibly absorbing hydrogen. These hydrides are very useful because the can be used for hydrogen storage for fuel cells or other hydrogen consuming engines. The non-hydride metal can absorb hydrogen by cooling the material to a suitable storage temperature and putting it in a hydrogen rich atmosphere under a high pressure. The hydride is then stored until more hydrogen is needed. Then it is heated to release the hydrogen to a delivery system that utilizes it. Examples of metals that can hydride are LaNi5, ZrV2, Mg2Ni, etc.. However many metals don't readily store hydrogen. They need to be pretreated first. This pretreatment involves removing oxide films on the metal's surface or fracturing some of the particles to expose un-oxidized surface of the material for hydrogen absorption. The way to do this is by cooling the particles, pressurizing with hydrogen, heating, and depressurizing the particles to chemically remove oxide barriers for hydrogen absorption. This process often needs to be repeated. US patent 7,700,069 Activation of metal hydrides by Robert D Stephens looks into finding a method of activating metal hydride that is less costly and less time consuming (Stephens, 2010).

Activation of the metal hydride is done by dispersing metal partials in an inert non-oxidizing liquid. The particle-liquid mixture is then subjected to "cavitation" by a suitable cavitation actuator. Cavitation is the abrupt formation and collapse of low pressure bubbles in the liquid, usually by mechanical forces. An Ultrasonic generator is often used to create the cavitation effect and the liquid must be able to tolerate the energy generated by the ultrasonic generator. This generator is used in conjunction with the cavitation vessel to create ultrasonic frequency vibrations in the cavitation mixture in the vessel. The cavitation of the liquid is carried out to cause elimination of the oxide coating on the surfaces of the particles. This process can also fracture particles on the hydride surface so to expose fresh particles for hydrogen absorption and release. The jets break old particles thereby increasing the surface area of the alloy. Suitable liquids for this procedure are supercritical carbon dioxide and liquid nitrogen. These liquids necessitate containing vessels that can keep them at the right temperature and pressure for cavitation. The advantage of using these liquids is that that readily vaporized from the activated metal or hydride particles. Other possible liquids include non-aqueous, organic liquids that allow cavitation at ambient temperatures. The liquid should not adversely affect the particles of the metal alloy during the cavitation process and the liquid must be easily removed from the particles. At the conclusion of cavitation activation of the particles, the liquid can be removed from the metal particles that are now ready for hydrogen absorption or release (Stephens, 2010).

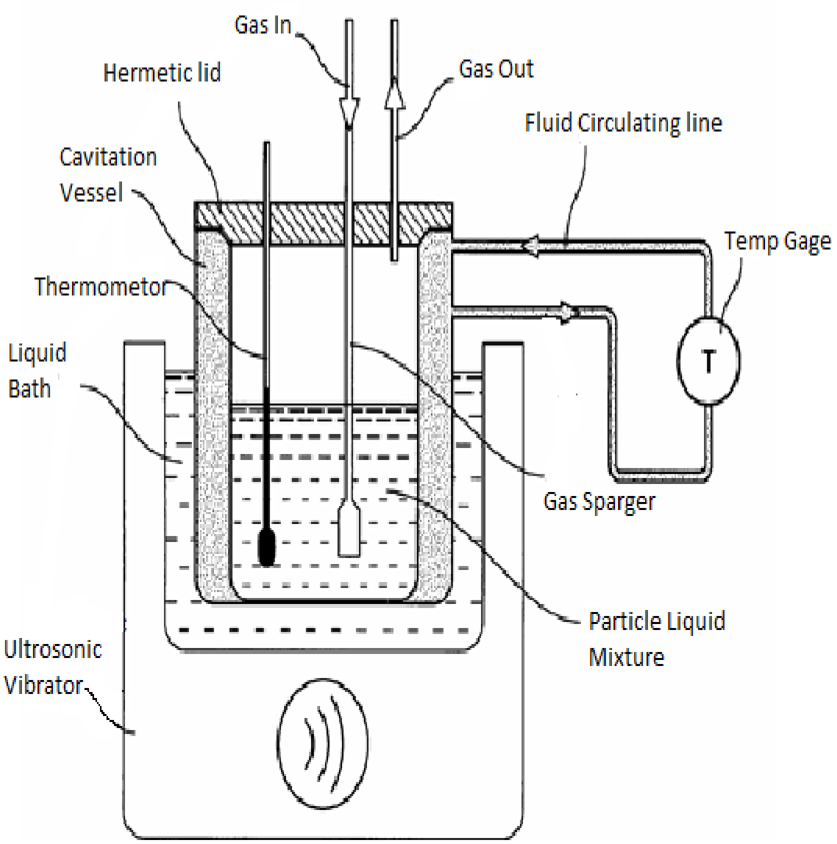


Figure 3.7: Laboratory Cavitation Apparatus

(Stephens, Robert)

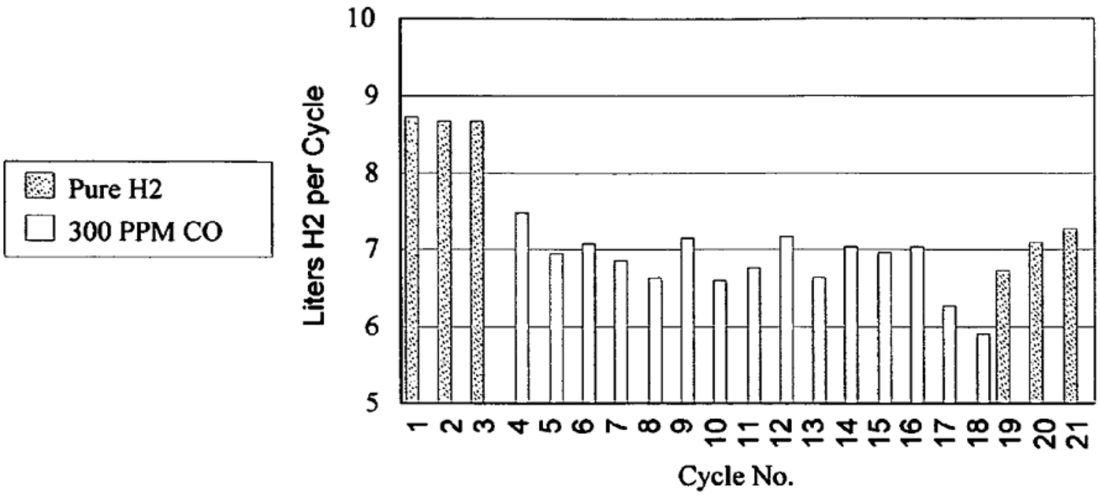
Figure 3.7 illustrates a laboratory cavitation apparatus using an ultrasonic generator to induce cavitation. The apparatus's parts include an ultrasonic vibrator container with a liquid bath for broadcasting ultrasonic vibration energy. A metal hydride particle-liquid mixture is contained within cavitation vessel and the top of the vessel is closed with a hermetic lid which permits a pass-through of thermometer and a gas sparger for a gas inlet, and gas outlet. The elective gas inlet and gas outlet may be used for providing a protective gas atmosphere, for example argon, over the contents of the cavitation vessel. The inlet and outlet may also be used for the initiation or removal of hydrogen to the vessel. The

Cavitation vessel is jacketed, and the temperature control of vessel is accomplished using thermostat-controlled fluid circulating lines. This apparatus makes the activation of the metal hydride possible (Stephens, 2010).

Even though this is an easy, cost effective way to activate Metal alloys it would be even better to prevent the need for this. Hydrogen, when produced, often has impurities that need to be removed before it can be used for its purpose. This includes being used in Fuel Cells. Hydrogen most commonly is produced today using steam reforming so the most common pollutants are water vapor, carbon monoxide, carbon dioxide, methane, and nitrogen. Carbon monoxide is the worst of these because it can damage metal hydrides and electrode catalyst used in fuel cells. The table shows a significant decrease in the hydride's hydrogen capacity. These pollutants interact with metal hydride in a variety of ways. Oxygen and CO affect the hydride's ability to collect hydrogen by reducing its capacity. These impurities also slow down the hydride process by forming weak bonds with the metal that stand in the way of the hydrogen. Water Vapor is the most common contaminant. When hydrogen formation begins, it flows towards the metal alloy carrying water vapor. The water vapor accumulates on the metal slowing hydrogen absorption. Oxygen can also form bonds on the metal's surface impeding hydrogen absorption. These reactions can also react with the hydride creates a very stable alloy that can't reversibly hydride easily. Methane, nitrogen, ammonia, and noble gases don't react with the metal alloy but if present in a large quantity could create a blanketing effect on the metal. This blanketing effect slows hydrogen intake to almost a halt. Table 3.5 shows the effect of CO on metal hydride over many cycles of use. The table shows a significant decrease in the hydride's hydrogen capacity (Golben, 2010).

Table 3.5: Hydride Capacity after being exposed to CO

(Golben, Peter)



Presently hydrogen is purified be platinum alloys, water scavengers, or filters that hold contaminants while letting hydrogen pass through. These methods work well but are high cost and can only be done in a stationary distribution stations. Another problem is that quality could vary from distribution center to distribution center. A possible solution to this problem is having a simple, compact, and mobile system for the purification of hydrogen. This concept is looked into in US7,736,609-Hydrogen purification system by Peter Golben. This invention presents a way of purifying hydrogen involving the use of hydride and a catalytic converter with a process controller. The process controller handles a series of check valves that open to release the contaminants from the hydrogen gas. This system is simple and portable and can be used in motor vehicles or in distribution centers. It is also very inexpensive because there is no need for items such as filters or scavengers. In addition the energy requirement is very low because the heat capacity is preserved as the high temperature heat source recirculates through the system. This novel system is compatible with all advanced hydrogen production systems including, but not limited to, photobiological production, PEM electrolysis, pyrolysis, or sodium borohydride production (Golben, 2010).

This invention requires that the hydrogen be pre-treating prior to compression by a catalytic converter. In this devise, CO and CO_2 are converted to methane and water vapor before it enters the hydride bed in the compressor. They are seen by the hydride alloys as inert gasses suggesting that they can be removed from the hydrogen stream during gas venting. The concept of compressing CO and CO_2 into methane is well known but combining that with a hydride compressor and letting the gas venting with heat recovery of the gas in the catalytic converter, fluid, and ambient fluid streams of the hydrogen compressor are not. This invention provides a method that can reduce hydride degradation as a result of poisoning by carbon monoxide and carbon dioxide which could affect equipment downstream, like fuel cell electrode catalysts. This system also eliminates the need for any other removal method such as “pressure swing adsorption processes.” The energy requirement for the hydrogen purification can be reduced through the integration of the compressor's closed loop heating-cooling system with a catalytic regenerative heat exchanger. In addition, the system can be made at low cost since all the components are inexpensive (Golben, 2010).

The catalytic converter is comprised of a first tube and a second tube located in the center of the first. These tubes can be made out of any material that can withstand the process, such as stainless steel or aluminum, and the size of each tube can vary depending on the capacity of each tube. In each of the tubes there is catalytic material, different in each tube. The material found in the first tube is located between the inside wall of the first tube and outside surface of the second tube. This material converts the carbon monoxide into CH_4. The material used by the inventor is a mixture of molecular sieve, palladium, and platinum. This mixture is then mixed with palladium on Al_2O_3. This is not the only material that can be used. The Patent goes on to say that any metal that will react with the carbon monoxide but doesn't oxidize will work. The second tube burns the vented, contaminated hydrogen stream to create the heat required to keep the bed at 300°C or more. This tube contains palladium as its catalytic material. The contaminated hydrogen is then sent to the catalytic converter at a temperature of 300°C. The stream is then sent to the counter flow heat exchanger to regain the heat value and then is sent to the hydride compressor or fuel cell (Golben, 2010).

Testing of this invention shows a lack of hydride degradation compared to hydride compression without it. During CO testing, the compressor alloy was checked periodically checked by Pressure-Composition-Temperature isotherm tests which showed that the compression alloy was able to maintain its performance over many cycles. The composition of the compressor discharged was also looked at. Without the CO converter, 300 ppm inlet concentration of CO results in 250 ppm outlet concentration. The passive purification system only converts about 50 ppm of CO into CH_4. The present invention results in the reduction of the CO concentration to the 10 ppm necessary to protect a fuel cell catalyst. Most of the CO is converted into methane and is released in large amounts (about 1000 ppm) with inert gas venting at the beginning of each cycle. The momentary opening in the valve sweeps away all the methane while only releasing a reasonable amount of the hydrogen stream. The vented gas is then recycled back to the hot water heater to regain its heat value. This test was also done with an initial CO concentration of 1000 ppm and this method was able to remove the CO to 5 ppm which is safe for fuel cell catalysts (Golben, 2010).

The impurities that come with hydrogen production can cause damaging effects to metal alloys or fuel cell. These impurities include carbon dioxide, carbon monoxide, water vapor, methane and other gasses. They can effect metal hydrides by decreasing there hydrogen capacity or can slow the hydrogen uptake process to almost a halt. They could also damage fuel cell catalysts. This is the reason why it is beneficial to remove theses impurities form the hydrogen gas. Hydrogen is currently being purified with the use of Palladium alloys or selective filters, or oxygen and water scavengers. These methods are very expensive and are limited in that they can only be used in stationary distribution centers. Finding a cheaper, more versatile method of hydrogen production would be beneficial for the hydrogen economy. This invention is offering a way of doing this. It provided a way of purifying hydrogen by significantly reducing the contaminants and made it possible to make it mobile and able to be used in a vehicle. This invention removes the need to activate hydrides which makes the whole process cheaper and more efficient (Golben, 2010).

A main part of the hydrogen economy is the distribution of hydrogen to the end user. Some of the routes to do this are by road, pipeline, air, sea, or even onsite manufacturing. Today, liquid and compressed hydrogen are being transported by tanker trucks but this method is very limited. Natural gas has been transported by pipelines for a long time and those same pipelines could be used to transport hydrogen. These pipelines are made out of steel and can withstand a pressure of 10-20 bars which is exceptionally suitable for hydrogen. These pipelines would need to be modified for hydrogen and would be more cost effective than installing new pipelines. Special ocean tankers have been designed to carry liquefied natural gas for many years and this could be done with hydrogen as well. Fuels haven't been known to use air travel to get to a destination but hydrogen has an advantage in being much lighter than fossil fuels. This could cut down on time and the evaporation of hydrogen. All of these methods are possible to transport hydrogen and make the hydrogen economy a reality (Mintz, 2002).

Hydrogen is one of the main contenders for the future energy needs of mankind. The hydrocarbon economy that we live in presently is unsustainable and has many disadvantages to it; one of these things being its contribution of CO into the atmosphere which is considered one of the main causes of Global Warming. Another disadvantage is that the world's supply of hydrocarbons, such as oil and natural gas, are becoming depleted and are not renewable. Therefore, it is essential that a new energy source is found.

Hydrogen is the most abundant element in the universe, making up the majority or all the stars but unfortunately hydrogen gas (H_2) is not found naturally here on earth [University of California, 2003]. It is found as a part of water and organic matter but hydrogen's energy cannot be harnessed without extracting pure hydrogen from them. Consequently, hydrogen production is an important part of making hydrogen fuels a good candidate for a replacement energy source. There are many ways of making hydrogen including Steam Reforming, Electrolysis, and Water Splitting but the most promising way of producing hydrogen is the use of microbes. Many microbes produce hydrogen from the natural metabolic processes. Even though hydrogen producing bacteria occur naturally, there is a need to be able to produce them in such large quantities that they could be industrially useful. Another problem is that while there are hydrogen producing organisms there are also hydrogen consuming organisms. These hydrogen consuming bacteria make it difficult to capture the hydrogen that is produced. Research is being done like the two inventions previously examined, and more research needs to be done to make hydrogen a viable source of energy (Hansen; Dae-Yeol, 2009).

Hydrogen storage is another issue facing the Hydrogen Economy. There are many ways of storing hydrogen but they all have their disadvantages. These disadvantages include being big and bulky, being too expensive to be practical, or can be susceptible to explosions. One of the inventions reviewed on this subject looked at liquid hydrogen tank and found a way to minimize hydrogen leakage. This was done by using a pressure management system to regulate hydrogen release when the pressure is at its critical point (Immel, 2010). This invention greatly improved the maintaining of hydrogen as compared to conventional hydrogen storage tanks.

The Hydrogen Economy is also looking at Metal Hydride to solve its hydrogen storage problems. Metal hydrides are elements, alloys, or intermetallic compounds that have the chemical property of reversibly absorbing hydrogen. These hydrides are able to store a large amount of hydrogen in a small area. Another advantage is that hydride is considered much safer than elemental hydrogen (Cutler, 2008). One of the problems looked at is that these metal hydrides can become contaminated and necessitate being cleaned. A cavitation apparatus was devised to be able to clean these hydrides and return to them their ability to absorb hydrogen in large quantities (Stephens, 2010). Another invention developed a way of purifying the hydrogen before it got to the hydride thereby reducing the chance of the hydride becoming contaminated. This will save on cost and time thereby making the process more efficient (Golben, 2010). Hydride could be the most suitable way to store hydrogen but more research needs to be done.

Other aspects of the hydrogen economy that are helping it progress is the making of Hydrogen Highways and the use of hydrogen in fuels cells. A hydrogen highway is a stretch of road that contains hydrogen fueling stations running a long it thereby promoting the use of hydrogen vehicles. In the United States, California was the first to adopt this idea. The Californian hydrogen Highway has done so well that other states such as New York and Florida are already in the process of developing their own hydrogen highways (Bensinger, 2008) (Addison, 2007). Fuel cells can be a very versatile producer of energy. In addition to cars and other vehicles, fuel cells can be used as a heating source for homes, an energy source for buildings, and can be used to power small handheld devises (Woodbury, 1997). All of these are possible if we find a way to efficiently produce hydrogen.

There are many problems that stand in the way of hydrogen becoming the main source of energy of mankind. These problems include hydrogen production, hydrogen storage, and even hydrogen distribution. Ways to solve these problems are coming out more every day but more research in the matter needs to be done to overcome these obstacles. If we are able to do this, hydrogen can become an endless supply of energy for the world.

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Chapter 4 MFC

The microbial fuel cell (MFC) in one format or another had been around for decades. It has only been in the last decade that significant advancements have been made allowing the MFC to come off the laboratory bench and into field research. In its basic operation the MFC consists of an anode and cathode, which harness electricity from digestive processes of bacteria.

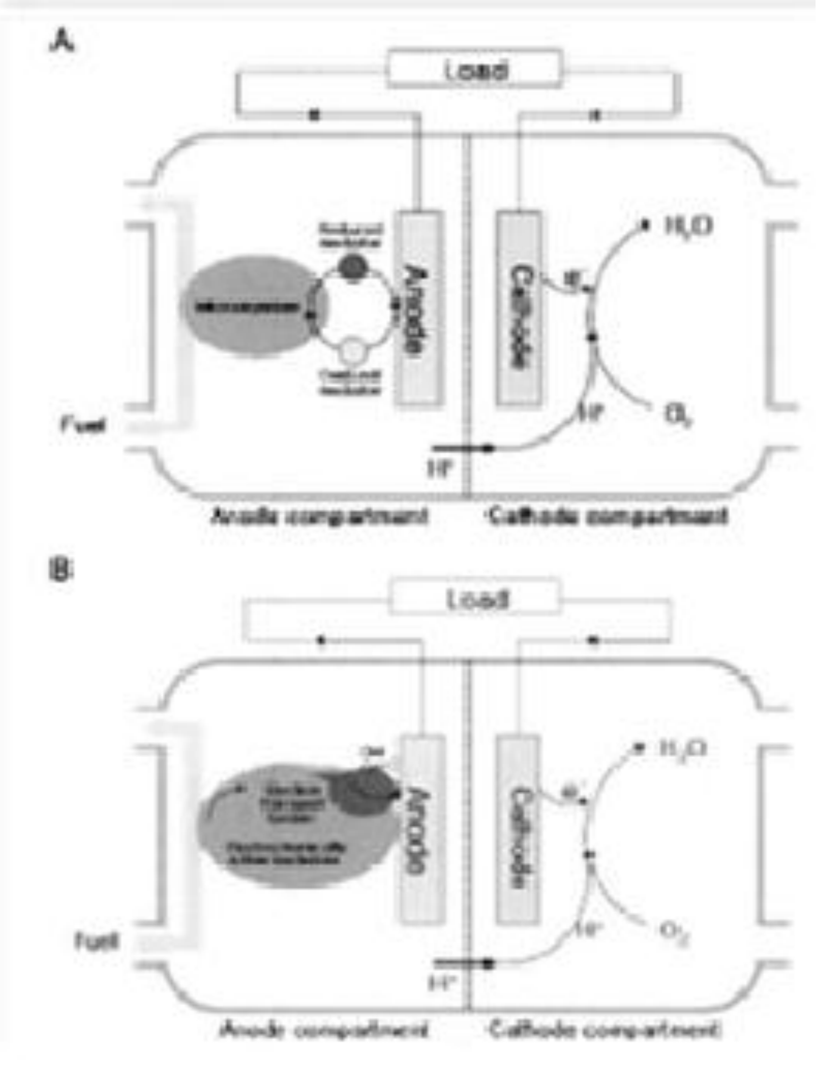


Figure 4.1: Two microbial fuel cell systems

(Chang 2006)

Early MFCs used electrochemically inactive microbes, which required the use of a chemical mediator, to transfer the electrons from the cells membrane to the MFC's electrodes. This process caused the mediator to be reduced during metabolic oxidation of the organic fuel and re-oxidized at the anode (Chang, 2006). These mediated MFCs allowed the use of most any bacterium, and also could use a wide range of mediators. Commonly used mediators included thionine, viologens, methylene blue, and a variety of other hydrophobic compounds. These chemicals were expensive, and the high concentration required for an efficient mediated MFC created a toxic environment for the microbes as well as toxic waste material.   Due low power generation, toxicity and costs any commercialized effort of a microbial fuel cell was impossible until mediator-less MFCs were developed.

The first mediator-less MFCs was created by Byung Hong Kim at the Korean institute of Science and technology; Patent # 5976719 was granted in 1999. The essential change in operation of a mediator-less MFC was the use of electrochemically active bacteria. The electron exchange of these bacteria occurs outside the membrane of the cells, allowing electrons to be transferred directly to the electrodes. Not only was the price and toxicity of the mediator eliminated but a more efficient MFC was developed. The direct contact of electrode the bacteria drastically reduced the internal resistance of the fuel cell. This particular patent used the bacteria *Shewanella Putrefaciens* that have cytochrome in the outer membrane which transfer electrons generated from oxidation of organic matter. These electrons are used to reduce ferric ions (Kim, 2006). The energy of metabolism is not used by the bacterium, but instead by the reduction of the ferric ion found as a coating on the anode. The inventors claim also that the sludge and methane produced in MFCs is greatly reduced without a mediator and the efficiency is increased. The inventors also used a variety of fuel sources such as: waste water (containing organic and inorganic matter i.e. Metals), acetic acid, lactic acid, pyruvic acid, propiaonic acid, valeric acid, alcohols, and an aromatic compound (toluene, phenol, cresolm benzoic acid, benxyl alcohol, benzaldehyde). This specific invention took advantage of multiple MFC layouts. The first used graphite rods as both electrodes being separated by sintered glass resulting in low effective elctrode surface area and a very high internal resistance (above 50 kΩ). Used graphite felt (higher surface area of 0.47 m^2/g) for the electrodes, which were separated by a cation-exchange membrane, which reduced resistivity of the fuel cell. The inventors also took advantage of a conventional electrolyte such as a phosphate buffer solution containing potassium chloride; this is flowed through the cathode chamber along with air. The anode chamber uses a similar electrolyte, but the chamber is in anaerobic condition with nitrogen flowing into the compartment before operation to remove all oxygen. The bacteria are cultivated in the anode chamber in anaerobic conditions. Though this initial mediator-less MFC eliminated the toxicity and expensive costs associated with earlier fuel cells, the power produced was still not suitable for commercial use.

Microbial fuel cells of the early 21st century appeared to have little practical use in the area of power generation. It may appear that these fuel cells, while an environmentally friendly way of making power aren't as cost effective as wind and solar energy production.

Research is currently being driven by another unique property of the MFCs, by using wastewater as feedstock, if properly tuned, clean drinking water is produced alongside the small power generation. Worldwide over 2 billion people do not have properly sanitized water because of the high startup costs of proper sanitation facilities. The United States dedicates approximately 4% of our power output into the water sanitation industry (Logan and Regan, 2006). A water purification system which produces power as a by-product cleaning water such as an area of great interest especially in countries lacking existing purification systems. It is because of this ability to both produce power and sanitize water that MFC research continues. It is also estimated that wastewater has approximately 9.3x as much energy as required to treat it. Though currently large-scale water treatment facilities are not economically feasible with current MFC technology, but as fuel cell technology is developed and emerging fields like nanotechnology may offer solutions in the foreseeable future. A large portion of costs and energy that goes into water purification is involved in the removal and processing of the left over sludge from the impurities in the water. It is evident that smaller scale MFC based water purification systems will be used for rural location water purification as well as energy production in that location.

Rural applications such as sensor stations require low power delivered over a few years. Sensor stations used in a variety of research fields such as volcanic exploration, deep sea or isolated areas near streams or ponds, even in the human body.

MFCs have been considered as battery replacement for existing medical technologies. Miniature implantable medical devices have been around for quite some time, but the primary problem of sustainable power has not been solved. Pacemaker batteries last between 5-8 years while, artificial hearts require external battery packs. Implantable MFCs, patent # 7160637 made possible with micro manufacturing techniques, these MFCs are powered from glucose, or other fuels from the bodies' fluids. This fuel cell uses the microbe *Sacchoromyces cerevisiae,* more commonly known as baker's yeast. Table 1 below shows half reactions outlined in patent application.

Table 4.1

Anode half reaction	Cathode half reaction
$C_6H_{12}O_6+6H_2O$ -> $6CO_2+24e^-+24H^+$	a. $4Fe(CN)_6^{3-}+ 4e^-$ -> $4Fe(CN)_6^{4-}$ b. $4Fe(CN)_6^{4-}+ 4H^+ +O_2$ -> $4Fe(CN)_6^{4-} +2H_2O$

As evident in the half reactions, ferricyanide ions are used as the oxidizing materials found on the cathode. The patent also points out to be useable in a biological environment, materials such as polysaccharides, porous silicon, and PTFE will be implemented as to not cause unwanted rejection of the implant. While the tested fuel cell of the invention uses the less efficient mediator based fuel cell, implementation of electrochemically active bacteria can eliminate the mediator resulting in a more efficient less toxic fuel cell. The tested model using methylene blue mediator had an average voltage over a test of 343mV. In its infancy the concept of an implantable fuel cell shows the flexibility of MFCs in isolated environments.

Physical construction of MFCs is a crucial variable in electrical production and water purification. In its simplest form MFC is constructed from its physical container, cathode and anode, which may or may not be separated by an ion exchange membrane. The physical container determines the volume of the cathode and anodes chambers. The construction also determines the spacing between the electrodes, nearer electrodes reduces resistances. The form can vary from boxes with anode and cathode on either side, or concentric rings anode inside with the cathode outside. Cheap simple MFCs can be built without an ion exchange membrane, but over time this results in contaminations of either chamber. The membrane can allow ions created from the digestion of organic materials to pass from the anode to cathode chamber but, restricts oxygen and cathode catalysts from passing. Anodes require a high surface area, which allows more microbes to digest the organic fuels, while also using a low resistance material. Graphite is one such material, available in graduals, sheets, rods and cloth, as well as carbon nanotubes (CNTs). Carbon nano-tubes give the highest surface area as well at highest cost; cloth too provides a high surface area, not quite as expensive as CNTs. Graphite Graduals or spheres or collections of thin sheets and rods provide the lowest cost solutions but at reduced surface area. Cathodes do not require as high a surface area for the oxygen half reaction to take place, but catalysts play a vital role in achieving a commercialized MFC.

Physical configuration is an important variable in designing a maximum output MFC. The volume of the anode and cathode chambers compared to the surface area of the electrodes is critical. A small fuel cell capacity can lead to greater energy densities (watts/m^3). For instance a 1cm^2 cell has been reported to produce 2.2kW/m^3, while a larger, at > 1m^3, efficient fuel cells will only produce 28W/m^3. While the overall power from the larger cell is greater than the smaller cell, its power density is significantly smaller. Other key factors include keeping the anode cell aerobic, as many electrochemically active bacteria can only survive short periods in anaerobic conditions. Conversely the cathode chamber requires an anaerobic environment for the oxidation half reaction to occur. Ionic membranes serve the purpose to separate the two chambers, while allowing only ions to pass through.

The research paper Engineering Microbial Fuel Cells: Recent patents and New Directions covers emerging technologies in recent years; specifically it discusses the development of layouts of MFCs through the years. Commonly used is the “upflow” layout of the cell. The up flow layout dictates that fluids containing the fuels enter through the bottom of the cell, while the effluent exits at the top. Figure 4A shows a membrane-less design that uses glass wool and beads to separate the cathode and anode chamber. The glass wool and beads offer a low resistance barrier (as it is a membrane-less MFC) that reduces mixing of each

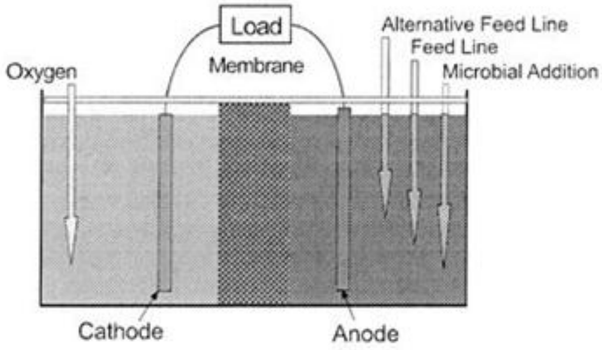


Figure 4.2: Fundamental layout from first MFC design patent

(Biffinger and Ringeisen. 2008)

chambers microbes or catalysts. By placing the cathode on top of the anode, the fuel cell pumps oxygen into the chamber, without it contaminating the anode. Figure 4.3 A shows a U shaped cathode chamber, this allows catholyte, enzymes or other bacteria used to increase output, to flow in the cathode chamber isolated from the anode.

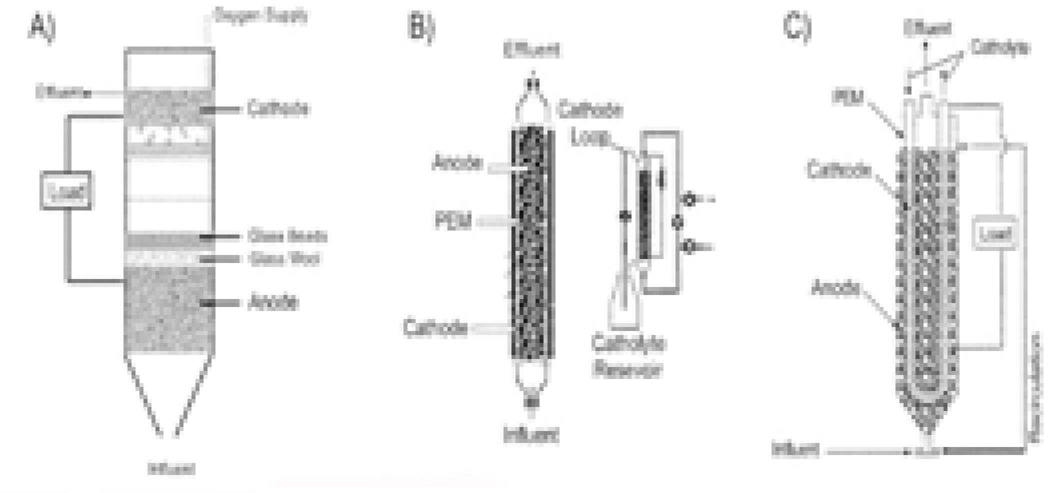


Figure 4.3: The independent up flow MFC layouts ((Biffinger and Ringeisen. 2008)

The other layouts maximize surface area to volume by using a cylindrical anode chamber surrounded by a membrane and cylindrical cathode. This cylindrical layout allows the ion membrane barrier to touch electrodes, resulting in higher efficiencies. This concentric design places the cathode in air, while isolating the bacteria in the anode chamber from oxygen. This design is seen in figure 4.4 below; 4.4 A shows off the cross section of the assembly (see Anion Membrane section for description of hydrogel with membranes). Figure 4.4 B shows the full MFC assembled, the inlet port is found at the top, the black seen through the perforated plastic tube shell is the graphite cathode; A top view of the anode is seen in 4.4 C, the many small holes are drilled to increase surface area in what would otherwise be a solid graphite rod. The straight tubes offer the advantage of increased flow, but with less surface area. This design could easily be lengthened, or implemented into a sub-cell MFC layout.

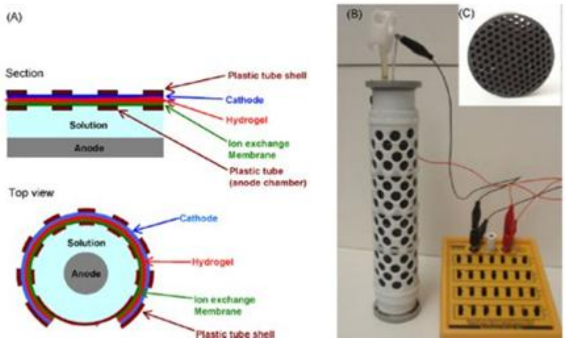


Figure 4.4: Membrane electrode assembly (MEA) A. Structure schematic, B. Photograph of tubular MFC, C. Photograph of cross section of monolithic carbon anode. (Kim, 2008)

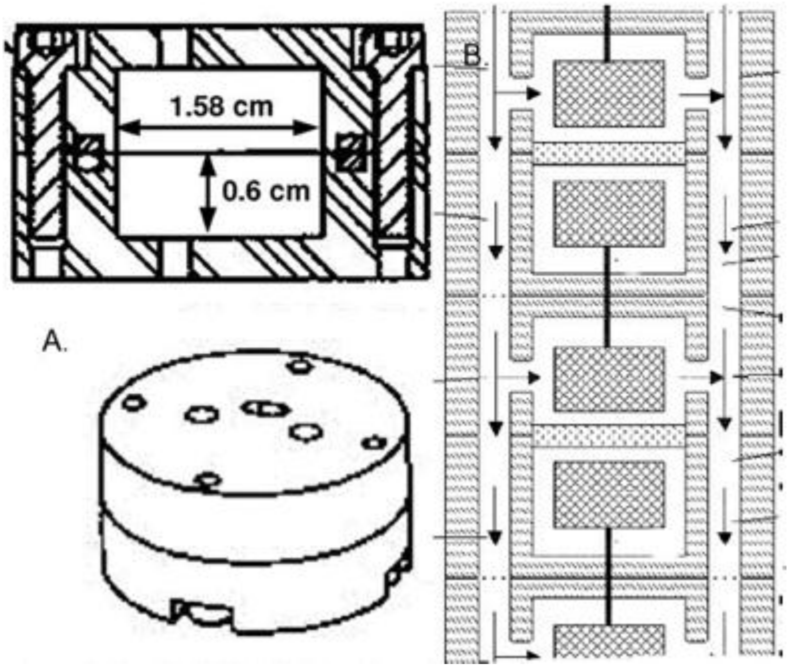
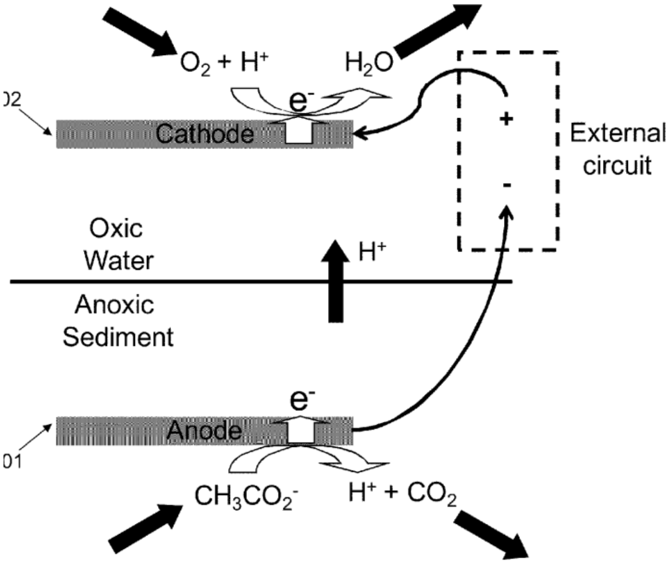


Figure 4.5: Patent #0048577, A. MFC sub unit cross section and isometric view, B. Multiple subunit cross section showing flow. (Ringeisen 2007)

The Patent # 0048577: Scalable micro fuel cells with Fluidic stacking capability, outlines a simple yet effective case design. Smaller fuel cells allow less efficiency to be lost through higher power densities, while giving the ability to construct larger systems to produce more power and process more water. These subassemblies are designed to have fuel flow through each sub cell. Seen in figure 4.5 B is a cross sectional view of multiple MFCs assembled; the fluid enters through the top, or bottom orientation is not vital. The rectangles in the middle illustrate the anodes connected with the black wire; the arrows illustrate the flow path for the effluent. Although this is the layout the inventors tested, its not limited to the exactly layout. A fluid path, which leads to systematic cleaning and digestion as the wastewater or other fuel as it flows from one chamber to the next, is included in these patent rights. Figure 4.5 A illustrates the size and layout of a sub-cell. The inventors state that many characteristics of their patents prototype do not offer high efficiency as the patent is related to the physical layout maximizing electrode surface area of the anode and pathway for protons to pass through membranes. Physical layout itself can be used with more efficient components: high surface area anodes, electrochemically active bacteria, and more efficient membranes. The patent states that the mini-MFC can reduce diffusion lengths by placing high surface area electrodes in a small volume chamber and gives the option of placing them in direct contact with the proton exchange membrane (PEM), with a wider surface area which also reduces electrical resistance. While in other layouts (Figure 4.2) the electrode is placed in relatively large volume chambers and placed several centimeters from the PEM; this results in decreased probability and speed of proton exchange to cathode increasing resistivity.

Another invention, the benthic microbial fuel cell allows a simplified layout for underwater applications. Benthic MFCs are utilized in oceans or rivers and can be deployed for years in low power sensor platforms. Benthic is a collection of organisms at the bottom of a body of water. The patent **Microbial Fuel Cell Power Systems,** #0081014, outlines a system utilizing a BMFC that uses a control system to charge batteries. The BMFC's, seen in Figure 6, anodes are placed in the anoxic sediment, while the cathode is in the anaerobic water. The system is specifically designed to power sensor systems, such as seismic sensors. Rather than relying on cultures of bacteria incubated on to the anodes, the system utilizes the microbes found in the sediment, which are naturally accustomed to its environment. Due to its simplicity, low power production, typically a continuous 0.4 V and 0.01W, provides a constant slow charging of the batteries which power the low consumption sensors which are not in constant use.

Figure 4.6: Patent # 0081014 Benthic MFC. (Tyce, 2010)



Another area of crucial research is in electrodes In MFCs electrodes of low resistance and high surface area are required; graphite cloth is commonly used to due relatively low cost to surface area allotted. Though many important factors such as spacing, bacterial treatments, and enzyme coatings are also vital for increasing fuel cell output. The layout of the MFC plays a critical role in determining spacing between the anode and cathode. Membrane-less fuel cell showed that power output is increased the closer the electrodes are. Spacing between electrodes was tested at 20cm, 24cm, and 28cm resulting in maximum power densities of 10.9, 8.6 and 7.4 mW/m^2 respectively. The same study concluded that a doubling of surface area resulted in a 28.6% increase in power and 40% for tripled surface area; this lead to the conclusion that there are other limiting factors in their membrane-less design. (Ghangrekar and Shinde, 2006). In MFCs utilizing membranes, some researchers have experimented placing the cathode and electrode onto the membrane as seen with a conductive hydrogel layer seen in figure 4.4

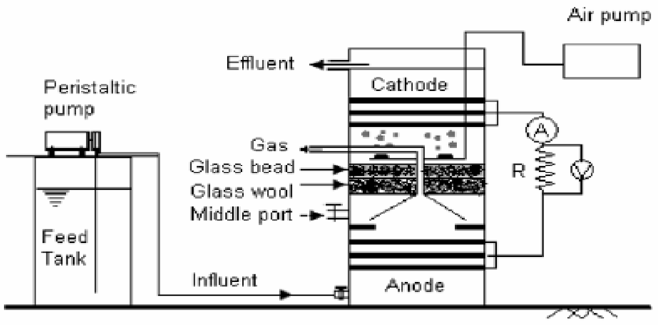
Microbial fuel cells operated with Iron-chelated air cathodes tests principal research was focused at cathode coatings, but the variable of anode thickness is also covered. In its initial layout the MFC had a 1.5 cm thick graphite cathode or 156cm^2 surface area. Increasing the thickness to 6 cm resulted in a power increase from 8.9 ± 0.4 mA to 22±1.0 mA. Current generation lowered dramatically, 16.4±2.6 mA when the thickness was expanded to 7.5 cm. (Alterman, 2009) Anode spacing and size play a large role in determining the efficiency, this study shows that larger MFCs don't necessarily produce more power, showing the value of stacked smaller fuel cells.

Biological and non-metal coatings are being analyzed as alternatives catalyst coatings, traditionally platinum, are being explored to reduce production costs and increase efficiency. Both nonmetal and biological coatings are areas of progress. Iron-chelated air cathodes stated that non-catalyzed support power levels up to about 11W/m^3. Compared to a platinum plated cathode (catalyzing the air half reaction) power density is increased from 115W/m^3. This 10 fold increase does not come cheap, as platinum's high price is a primary deterrent for commercial sized, efficient MFCs. Biological catalysts on the cathode have resulted in 83W/m^3 but the extra bacterial cultures make the cells unstable outside of lab conditions. Iron-chelated cathode study utilizes a Iron solution to act as an intermediary electron acceptor in the cathode chamber. By preventing a precipitation reaction of the ferric catholyte by controlling pH levels, it results in a stable operation. The study uses various iron-chelating molecules on carbon cloth. iron- Ethylenediaminetetraacetic acid (Fe-EDTA) chelated cathodes were found to be the best performing compared to FE-NTA, Fe Citrate and Fe succinate in aerated liquid cathodes. Though the study found that Fe-EDTA, a common chelating material, was not as powerful as a similar platinum MFC, the increased benefits from stable long term operation, lower cost and toxicity than platinum make this a viable option for commercial MFC (Alterman, 2009).

Cathode chamber biocatalysts are being explored as a cheaper alternative to platinum; A study on bio-catalyzed MFCs used Ferro/manganese-oxidizing bacteria. The cathode is treated with Iron and manganese oxides, and a secondary bacteria culture of *Leptothrix discophora* and *Leptothrix discophora*. A multi day bacteria culture start-up is required, this entails growing cultures on the cathode for days to hours before the MFC is at full power output. Optimization of iron and manganese quantities on the cathode are predicted to cut down on this start-up time. The growth of bacteria, digesters in the anode chamber and catalytic microbes in the cathode chamber, resulted in the lowering of the internal resistance from 40.2 Ω to 14.0 Ω. Much of this decrease is a result of the Fe/Mn-oxidizing bacteria enhancing oxygen reduction. *Leptothrix discophora* oxides Mn(II) to $Mn0^2$ releasing to electrons to oxygen. Though power outputs of this method are around $32W/m^3$, the benefits offered are affordable sustainable MFC power sources. Because this catalyst is based on microbes selective processes, or genetic engineering could allow produce efficient oxidizing bacteria could be utilized to better effect in an MFC (Yanping Mao, 2010).

MFCs can be built with and without ion membranes, both having pro's and cons. A membrane-less MFC is cheaper, as it removes an expensive element, as well as higher power output as a membrane separating the cathode and anode chambers causes an increase in resistance of the cell. This advantage of an increase in power is unrealistic in a real world extended application. The lack of membrane creates a single environment for the cathode and anode chamber as both halves mix microbes, air and catalysts. The aerobic environment required at the cathode shortens the life of the digester microbes that thrive in an anaerobic environment. Some of the problems can be alleviated with layouts similar to Figures 4.3 A and Figure 7. Membrane-less microbial fuel cells for water treatment have been shown to remove in 88% of contaminants in water treatment (Ghangrekar, 2006). The MFC was continuously fed with artificial wastewater at a rate of 5.011 L/day for 75 days. The schematic seen below (figure 4.7) illustrates the MFC used in this experiment; the separation layer shown between the electrodes is a glass wool and bead layer to reduce contamination. The air pump on top of the anode keeps its environment anaerobic, also the funnel shaped device vents any gases produced by the Bacteria in the anode chamber. Similar results have been seen in other studies with higher power output due to higher surface area electrodes as well as other variables previously discussed. One of the most commonly

Figure 4.7: Membrane-less MFC schematic. (Ghangrekar, 2006)



used ion exchange membrane is Nafion a DuPont product that was invented in the 1960’s. This product is an expensive component at $600 per square meter, driving up costs of MFCs considerably, existing commercial membranes off less or equal performance for around the same amount of money. In wastewater treatment application, sludge build up from waste found in the water can often lower the efficiency of the membrane. New membrane less resistive anion embranes would result in greater power as reduced resistance greater possibility and speed with which anions pass from anode to cathode chamber. Hydrogel (EGC gel formulated for EKG machines) implementation seen in figure 4.4 B is a more conductive material than the wastewater that separates the two electrodes, and the gel fills in gaps between the membrane and cathode, increasing surface area.

For a commercial grade MFC, the break through found in these patents and research papers need to come together to find a the right mix of cost vs. ability with material variables such as electrodes, bacteria, catalysts, membranes, and cell layout to provide clean drinking water. Inevitably these commercially available MFC water purification systems will lead to further advances in power output.

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Conclusion

In reading this, the importance for an efficient biofuel to replace petroleum is clearly stressed. As a way of making us less dependent on the use of petroleum, we must find and utilize products that are normally made with petroleum and instead produce them by means which do not need petroleum. A major everyday product this can be used in is plastics.

Petroleum based plastic production is not the most healthy way to create plastic. When plastic is manufactured many chemical pollutants are released into the air for anyone to breathe in. Also when petro – plastic is created, there is a chemical within it known as BPA. BPA is very dangerous, especially to young adults and children. BPA can mimic growth hormones in these individuals and cause major health concerns.

Plastic that is created from petroleum is not environmentally friendly. The plastic that is created, though strong, has many drawbacks. It is not biodegradable, and is expensive to produce. The production process is somewhat similar to that of PLA (poly lactic acid). The oil is refined, and turned into pellets, and then the pellets are melted and formed into plastics. Petroleum based plastic as previously stated degrade very slowly. This slow degrading process is due to the molecular bonds that petroleum based plastic posses. These strong bonds allow petroleum based plastic to oppose natural degradation for a long period of time.

Since 1950 one billion tons of plastic has been discarded. After 1955 recycling programs began to appear. These recycling programs allowed plastic to be re – molded, and created into usable items again. Recycling of plastics had proven to be a difficult process, because it is extremely difficult to automate the sorting of plastic making it labor intensive. With it being labor intensive it costs a lot of money to do.

There are increasing amounts of alternatives to petro based plastics appearing on the market. One of them being a veteran is called poly lactic acid (PLA). PLA is a type of bio plastic that is created from starches. Here in the US PLA is created mostly from corn starch. However in the rest of the world PLA is created from sugar cane and other similar starches. This is an expensive plastic to make, however it has become more affordable to create recently.

PLA is used for recyclable and biodegradable packaging. This includes bottles, yogurt cups, candy wrappers, food utensils, and trash bags. It is also used to make fibers that are used in clothing carpets sheets and towels. PLA is also used in biomedical applications used for sutures, prosthetic materials, and materials used for drug delivery. The uses for this bio plastic are very limited, due to the product reverting in less than sixty days.

PLA was discovered in the 1890's, and found its way to the market by way of biodegradable packaging. Even though PLA is bio degradable it cannot be composted in home facilities, even commercial facilities limit the amount of PLA composted due to its high acidity.

There are other forms of bio plastics on the market; however they aren't well publicized, due to the high cost, and average performance. Included in these are starch based products. These products are known as thermoplastic starch, and made out of what is known as plastarch material. This material absorbs humidity well, and is used within the pharmaceutical field in creating drug capsules.

Another bio plastic is referred to as (PHB) also known as Poly-3-hydroxybutyrate. The biopolymer (PHB) is polyester produced by a certain bacteria processing glucose or starch. The characteristics of (PHB) are similar to polypropylene. PHB produces a transparent film at a melting point higher than 130 degrees Celsius and is biodegradable without residue. This is even compostable at the home of the intended user of its products.

From performing this research I have found that there are many alternatives to petroleum based plastics. However there are drawbacks to these products. There is a high cost to produce them, and they are not as efficient as the petroleum based products. However the pollution created by the production process is far less than that of petroleum.

Knowing that the production of a biofuel allows for an everyday product like plastic to become independent of petroleum, it gives positive outlook to the future of further developing the buiofuel industry towards making us independent of petroleum. This knowledge also helps propel the research of finding an efficient way of creating and harnessing power from MFC. Along with mass producing hydrogen highways and further developing lignocellulosic material to better produce ethanol and butanol.

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