

HEAT OF COMBUSTION OF ALGAE FOR USE IN A DIESEL ENGINE

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## ABSTRACT

With nearly a quarter of the world's population living without any access to electricity or modern energy, strategies for providing energy are very important. While the use of fossil fuels can bring the much needed energy to these areas they come with a host of problems. Fossil fuel use contributes to greenhouse gas emissions, air pollution and ocean acidification. In many areas fossil fuels have to be transported in. The subsequent transmission and distribution can be difficult especially in rural areas. Dependence on fossil fuels also leaves the user vulnerable to disruption in deliveries and price fluctuations.

While there are many options for locally provided renewable energy, biomass is particularly attractive. Biomass can provide a clean, reliable and secure energy source. Almost every country has access to some sort of biomass. In choosing a biomass the criterion for selection should be: energy conversion yields, form of energy required and type of biomass available. Microalgae are good candidates because they use very little land, can use non-arable land, are easily adaptable to different growth conditions, and are very efficient solar collectors. Algae also have a near-continuous harvest stream and have less complex conversion processes than lignocellulosic biomass. Finding a way to use algae to provide an underdeveloped area its first electricity is very important. Although algae can be used to create biodiesel, methane, ethanol, and hydrogen these technologies are complicated and are still in the demonstration phases. This study explores if algae could be used directly as an alternative fuel in a diesel engine to create electricity. In this study a specific strain of algae was grown, collected, and desiccated before

using a bomb calorimeter to measure the heat of combustion. When this was done the algae was found to have an energy content of  $4471.2 \pm 95.1$  cal/g.

## DEDICATION

I would like to dedicate this thesis to my parents who have supported me throughout this master's program in every way possible.

I also want to dedicate this to my dear husband for always being encouraging and supportive and to my amazing daughter who inspires me to be the best I can be.

## ACKNOWLEDGEMENTS

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## LIST OF ABBREVIATIONS AND SYMBOLS

CH<sub>4</sub>, Methane

CO<sub>2</sub>, Carbon Dioxide

H<sub>g</sub>, Heat of Combustion

H<sub>2</sub>, Hydrogen

HNO<sub>3</sub>, Nitric Acid

Na<sub>2</sub>CO<sub>3</sub>, Sodium Carbonate

NO<sub>x</sub>, Mono-nitrogen Oxides

N<sub>2</sub>O, Nitrogen Dioxide

O<sub>3</sub>, Ozone

SO<sub>2</sub>, Sulfur Dioxide

W, Energy Equivalence Factor

Δ, Difference

## CHAPTER 1

### INTRODUCTION

In the 1880s the modern electricity industry developed. Over a 130 years later nearly one quarter of the world population, 1.6 billion, still lack access. This percentage has not changed since the 1970s (Ahuja & Tatsutani, 2009). In rural areas the percentage is even higher with over one half living without any form of modern energy (Moss et al., 2011). Instead of relying on modern fuels such as kerosene or natural gas rural areas rely on wood and charcoal as their source of energy. Most often these traditional sources of biomass are used in an unsustainable way. Just a small amount of electricity in these areas of underdevelopment can greatly increase the quality of life. Being able to charge cell phones, listen to radio broadcasts, and pump a minimal amount of drinking water are examples of how a little power can make a big difference.

Most of the world's energy comes from three sources: nuclear, fossil fuels and renewable resources. The majority of the energy is from fossil fuels in the form of coal and natural gases. With the exception of nuclear fission and hydroelectric power, these sources are finite and many agree will be used up shortly (WEC, 2010). The main sources of energy in the world are not only unsustainable they are also the primary sources of anthropogenic sulfur dioxide (SO<sub>2</sub>), carbon dioxide (CO<sub>2</sub>) and mono-nitrogen oxides (NO<sub>x</sub>) emissions (Patil, Tran, & Giselrod, 2008; Tonn, 2002). Along with climate change caused by these pollutants, other environmental concerns such as air pollution, forest destruction and acid rain are a definite threat to human and environmental security (Dincer, 2000) . The great need in the world to reduce pollution and carbon emissions

may at first seem at odds with the need for energy. This does not have to be the case if governments can look for solutions and policies that fulfill both these needs (Martinot, Chaurey, Lew, Moreira, & Wamukonya, 2002). In fact Moss et al. state that solutions can range from “extending existing grids reliant on carbon-intensive fuels to installing distributed systems and micro-grids, and employing renewable sources of energy such as solar” (page 2). Another example of this would be using biofuels that are sourced locally. In comparison with petroleum diesel, biodiesel can substantially reduce life-cycle greenhouse gas emissions (McCormick, 2007).

There is a tremendous need to have universal access to reliable, modern and safe energy. When trying to solve this problem of energy equity, the need for an energy source that is local and sustainable is vital. This problem raises a number of technical as well as ethical questions. In providing for the wellbeing and security of people through access to energy, how do we not endanger the wellbeing and security of others? Where do the funds come from that can be used to set up these infrastructures (Moss et al., 2011)? Even though there are many challenges it also provides a tremendous opportunity. It is possible to provide an area with its first modern energy from a clean and sustainable source. Instead of switching dependence from petroleum to renewable resource later, a sustainable model can be used from the very beginning (Ragauskas et al., 2006).

### Importance of Energy

People living without power have difficulty with many things that those living in developed countries take for granted. Lack of energy is linked to poverty, poor health, unemployment and population growth. There are also a lack of enterprise, education and

opportunities for women (Koppinger, 2007). Essential medical devices and vaccine storage require electricity. Also simple things like cooking that are done through traditional sources such as wood and dung expose users to hazardous pollutants. These indoor pollutants are responsible for two million premature deaths per year in many parts of the underdeveloped world (Moss et al., 2011). Just a little energy can also have a tremendous impact on food security. New sustainable livestock management methods have been developed that employ the use of a electric fence that is maintained by a 9 Volt battery (Salatin, 1995).

Having access to modern forms of energy is also vital in reducing the number of people living on less than the equivalent of 1 United States Dollar per day. It also improves access to primary education, promotes gender equality and reduces child mortality (Moss et al., 2011). Electricity can also greatly increase useable time by allowing light at night for studying. Pumped water can allow women more time for other activities because they are not carrying water great distances. It can also help push people out of poverty by allowing them to use computers and cellphones. Having access to radio can help alert populations of coming disasters. All of these items give tremendous economic opportunities and show that electricity in even a small amount is very important in alleviating much of the suffering and poverty throughout the world.

### Human Security

Human security is affected in many ways by not having access to energy and by using nonrenewable energy sources. Fossil fuels are a limited resource and eventually conflicts will arise over these finite resources. As the supply starts to dwindle the price will increase and those countries that rely heavily on these sources will be vulnerable. There have been shortages of oil and other fossil fuels in the past and this will inevitably happen again. If an area is reliant on

imported fossil fuel this leaves them vulnerable every time there is a shortage crisis. If a particular area is instead reliant on a local sustainable source they will be much less affected.

Many people with disabilities have special needs that must be met through energy. A diabetic may need to keep insulin cold. A person with multiple sclerosis has negative health consequences if they become overheated. In Australia a person with multiple sclerosis spends between 4 and 12 times more on keeping cool than the average household (Summers, Simmons, & Verikios, 2012).

## Climate and Environmental Changes

The earth's climate is a complex and dynamic system. Incoming energy from the sun, outgoing energy radiated from the earth, the exchanges of energy among the atmosphere and the exchange in energy among all the matter on the earth such as the oceans and land affect the earth's climate. The atmospheric composition is very important because it affects incoming solar radiation and the outgoing infrared radiation. Naturally occurring greenhouse gases such as carbon dioxide (CO<sub>2</sub>), nitrogen dioxide (N<sub>2</sub>O), water vapor, methane (CH<sub>4</sub>), and ozone (O<sub>3</sub>) all help warm the earth by stopping infrared heat energy from escaping into space. This is considered the 'natural greenhouse effect' and keeps the earth about 33°C warmer than it would be otherwise (WDR, 2009). This allows for water to exist in its liquid form on most of the planet and lets us enjoy life on earth as we know it.

The natural greenhouse effect can be amplified by human activities through emitting greenhouse gases by various activities. Globally averaged atmospheric mole fractions in 2011 reached new highs with CO<sub>2</sub> at 390.9±0.1 ppm, N<sub>2</sub>O at 324.2±0.1 ppb and CH<sub>4</sub> at 1813±2 ppb. Since pre-industrial times this constitutes increases of 140%, 120% and 259%, respectively

(WMO, 2012). As seen from figure 1 the greatest effect of anthropogenic greenhouse gases comes from the burning of fossil fuel. Deforestation and changes in land use are also having a great influence. The World Meteorological Organization states that CO<sub>2</sub> is the most important of the anthropogenic greenhouse gases and is responsible for 85% of the increase in radiative forcing (2012, page 2). As seen in figure 2 there is a correlation between increasing CO<sub>2</sub> levels and global increasing temperature. Also significant is the increase in CH<sub>4</sub> and N<sub>2</sub>O. About 60% of CH<sub>4</sub> comes from anthropogenic sources such as biomass burning, fossil fuel and rice agriculture. About 40% of total N<sub>2</sub>O emitted comes from anthropogenic sources such as biomass burning, fertilizer use and industrial processes (WMO, 2012).

Since preindustrial times earth has experienced a temperature increase of about 0.8°C. It takes decades for oceans to come into equilibrium with the increase in infrared radiation and so the full effect of the temperature increase from current levels of anthropogenic greenhouse gases has yet to be realized. It is estimated that the earth is already committed to a 2°C temperature increase (WDR, 2009). If the current use of fossil fuels is not changed the increase over the next century will be even greater. The effects of a warmer climate are extensive. It has been demonstrated that there is a direct link between a warmer climate and extreme precipitation events (Allan & Soden, 2008). It has also been suggested to cause flooding, hurricane intensity, and wildfires.



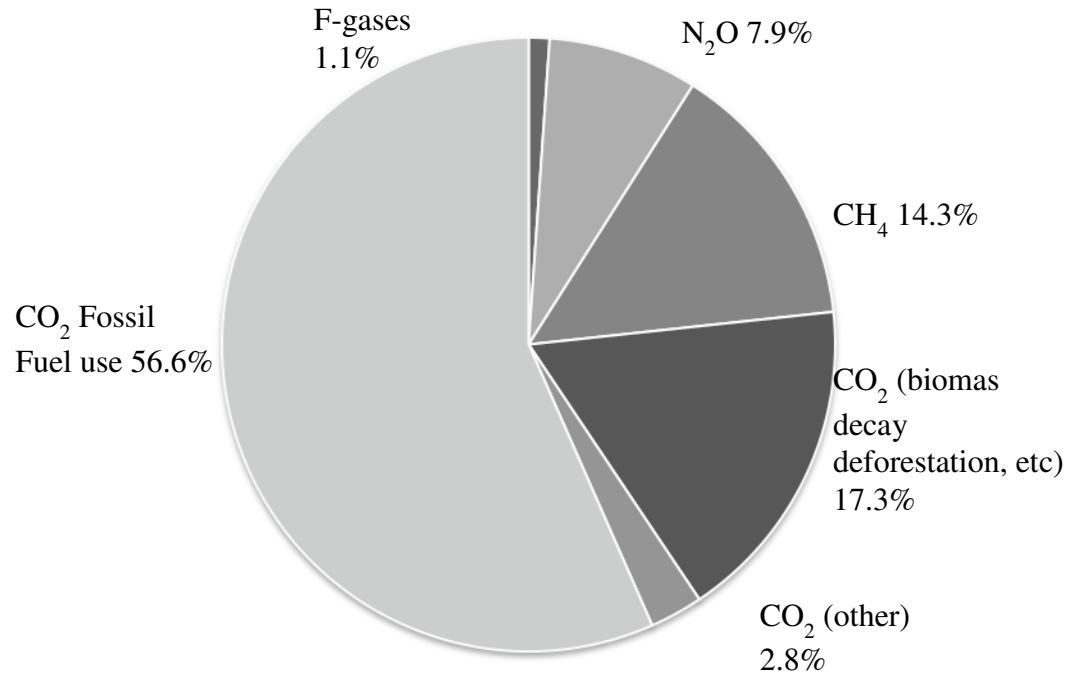


Figure 1 Global anthropogenic green house gas emissions in 2004. Adapted from (IPCC, 2007).

Along with climate change caused by greenhouse gases another problem generated by anthropogenic CO<sub>2</sub> emissions is ocean acidification. The oceans absorb CO<sub>2</sub>. When CO<sub>2</sub> enters the ocean it reacts with seawater to form carbonic acid. Since the beginning of the industrial revolution the ocean's average acidity has increased by 30 percent (Orr et al., 2005). The total atmospheric CO<sub>2</sub> is about 55 ppm less because of oceanic uptake (Sabine et al., 2004). Although there is limited understanding as to what the effects of this may be, it is assumed that marine biota such as coral reefs, bivalves, and calcareous plankton whose skeletons contain calcium carbonate will be affected (Caldeira & Wickett, 2003). There is a slow mixing time for the uptake of CO<sub>2</sub> into the oceans. Its is estimated that in 1000 years there will still be 17-33% of fossil fuel carbon in the atmosphere (Archer, 2005). Caldeira and Wickett state that "unabated CO<sub>2</sub> emissions over the coming centuries may produce changes in ocean pH that are greater than

any experienced in the past 300 millions years, with the possible exception of those resulting from rare, catastrophic events in earth's history" (page 365). When considering the deleterious effects of anthropogenic greenhouse gas, the acidification of the ocean should be a major concern.

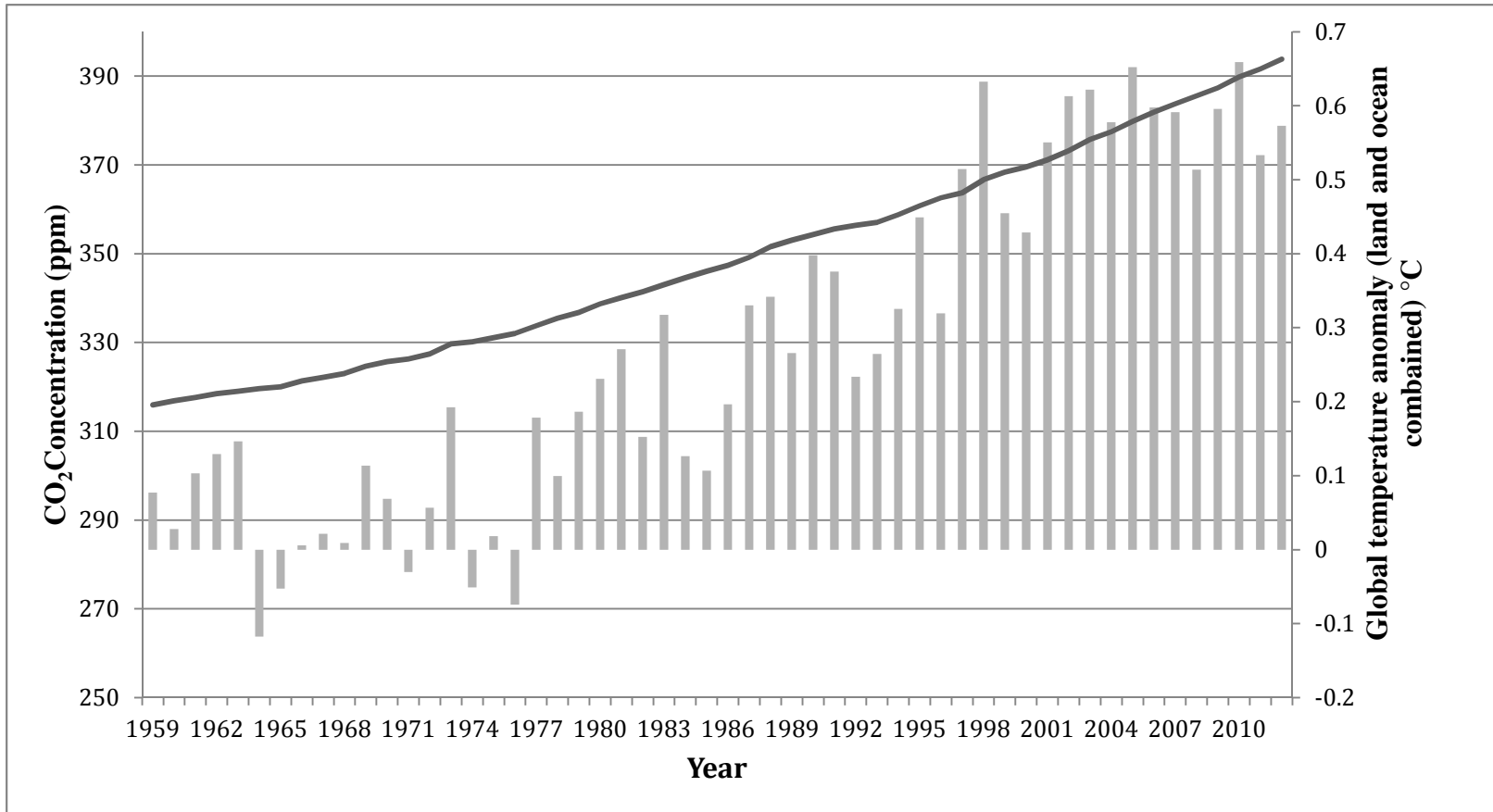


Figure 2 Global CO<sub>2</sub> concentration and annual average temperature anomaly. Data from (Tans & Keeling, 2013)

## Renewable Energy

Renewable energy is a type of energy that is naturally replenished so it is essentially inexhaustible and can be restored in a relatively short period of time. It also provides much lower greenhouse gases and other pollutants. Types of renewable energy are hydropower which is derived from flowing water; geothermal; biomass such as algae, wood and switch grass; solar; and wind energies (EIA, 2012). Renewable energy has great potential; in 2011 it accounted for only 9% of US energy consumption (EIA, 2011). Figure 3 shows where the U.S. gets its energy from as well as the percentage share of the different types of renewable energy. In the EU electricity from renewables has grown considerably since 2000 and was nearing 20% of consumption in 2010 (ECU, 2012). It is reasonable to imagine that a population's first source of electricity could come from renewable energy.

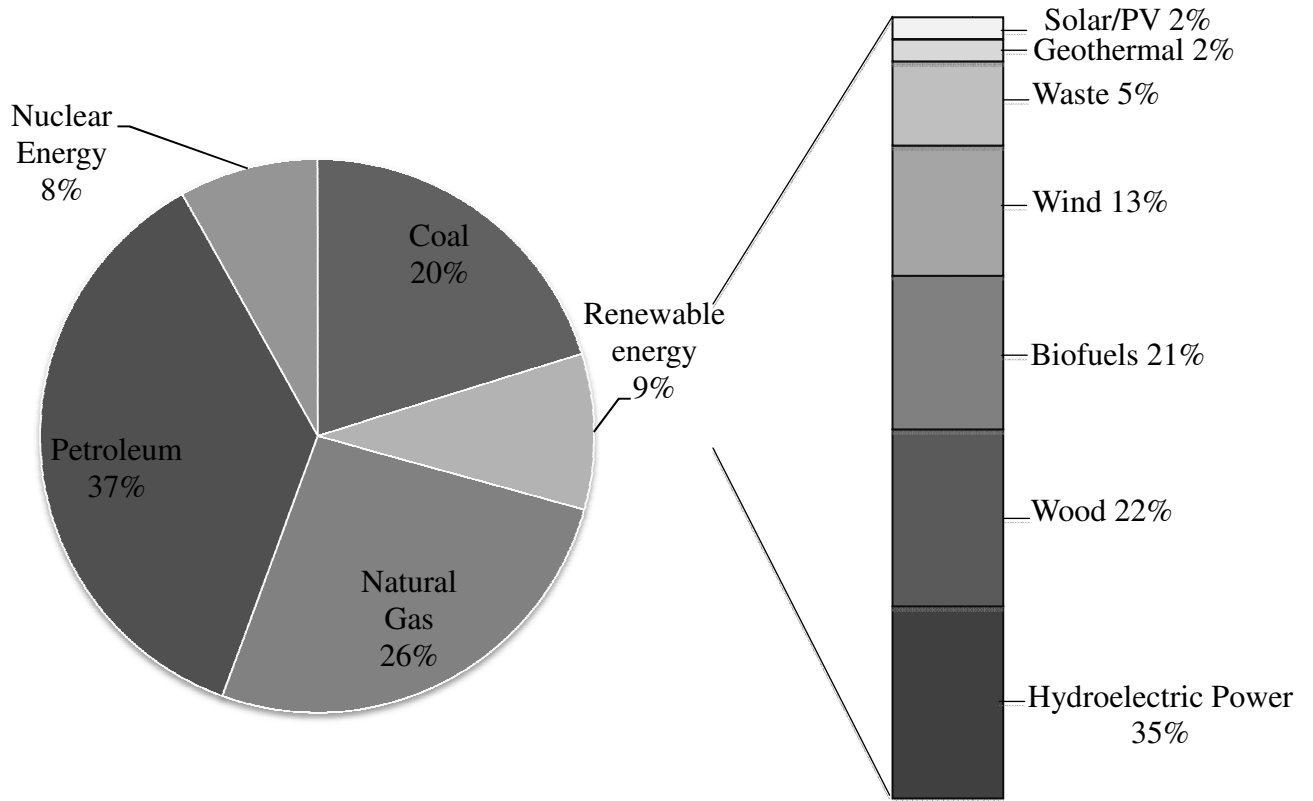


Figure 3 Renewable energy as a share of total energy consumption in United States. Adapted from (EIA, 2012)

### Importance of Renewable Energy in Underdeveloped Nations

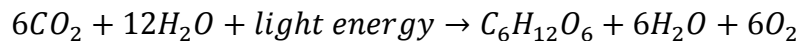
Providing energy to underdeveloped nations is not an end in itself but is a means to providing sustainable human development. Having energy from a renewable source will give a country human and environmental security. Nearly every place on earth has access to some source of renewable energy. Especially in rural areas, providing energy locally relieves the economic and technical hurdles of transmission and distribution of energy generated from far away (A. H. Demirbas & Demirbas, 2007). As a first step biomass provides a great opportunity because it can be grown as an indigenous energy source in most countries.

## CHAPTER II

### RENEWABLE ENERGY FROM BIOMASS

#### Biomass

Biomass is a renewable and very bountiful resource. It is essentially sunlight stored as chemical energy. Green plants convert sunlight to biomass by utilizing a reaction between CO<sub>2</sub> from the air and water by a process called photosynthesis. The solar energy the plant collects is stored in chemical bonds in the structural components of the plants. Ideally the biomass is processed efficiently in extracting the chemical bond energy so that the product waste is combined with oxygen and oxidized to produce CO<sub>2</sub> and water. The general formula for photosynthesis is:



From an environmental outlook this is beneficial because biomass absorbs the same amount of CO<sub>2</sub> during growth as it emits during combustion (A. Demirbas, 2004). Worldwide biomass supplies 10-14% of the world's energy supply (McKendry, 2002a). Biomass can come from natural processes such as wood and algae or through human activity in the form of organic waste (A. Demirbas, 2004).

The main components of biomass are lignin, cellulose, and hemicellulose. Lignin is a non-sugar, complex chemical compound that can greatly differ from plant species to plant species. It is mainly a polymer derived from coniferyl, coumaryl, and sinapyl alcohols (Ragauskas et al., 2006). Cellulose is a linear glucose polymer and hemicellulose is a branched

polysaccharide containing many different sugars but primarily five-carbon monosaccharaides. Cellulose is usually the largest fraction of plant material by weight at 40-50% and hemicellulose is about 20-40% (McKendry, 2002a). The rigidity of the plant species is related to the relative fractions of lignin; the higher the lignin content the more rigid the overall structure. When processing biomass for energy the fractions of cellulose and lignin are one of the determining factors for how it will be processed. As seen from figure 4, the majority of biomass energy currently comes from wood and wood waste (M. F. Demirbas, 2011). Man has been utilizing biomass for millennia as a fuel and for nutrition through sugars and starch. More recently in history fossil fuels have been used. It takes millions of years for fossil fuels to form from biomass and so considering the lifetime of man this is not considered a renewable resource.

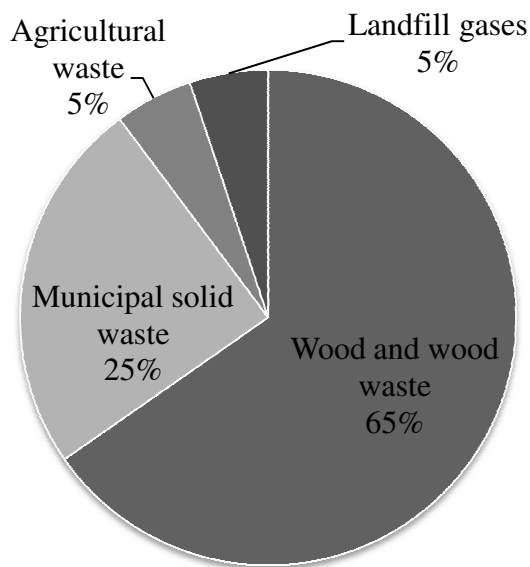


Figure 4 Sources of the world's biomass energy (M. F. Demirbas, 2011; Tsukahara & Sawayama, 2005)

## Energy from Biomass

There are three main energy products that biomass can be converted to: transport fuels, electrical/heat energy, and chemical feedstock (McKendry, 2002a; Stolarski, Szczukowski, Tworkowski, & Krzyzaniak, 2013). There are a number of ways to convert biomass into this useful energy. These can be classified into two main groups, biochemical and thermochemical conversions (figure 5). Thermochemical conversions include gasification, liquefaction, pyrolysis, and direct combustion. Biochemical conversions include fermentation, anaerobic digestion, and photobiological hydrogen production. The biochemical routes to energy utilize the metabolism of organisms and are generally more efficient when looking at organic matter and nutrient recycling. Although biomass can be converted to useful energy in all of these ways, 97% of the world's bioenergy comes through combustion (A. H. Demirbas & Demirbas, 2007).

The total or maximum value of energy available from biomass is equal to that source's caloric value, also called heating value or heat of combustion. This is measured by the combustion in air and is considered the energy content. The caloric value is usually expressed in energy content per unit mass or volume. For a solid this would be expressed as kJ/kg or cal/g. For a liquid this would be kJ/L and gases would be kJ/nm<sup>3</sup>. It is important to note that no matter how a biomass source is used the maximum energy available is the same. In practice the energy extracted can greatly differ from one conversion technology to another. The total net energy conversions are calculated from the entire conversion process. The caloric value for biomass is similar for all plant species and lies somewhere between 4000-5000 cal/g (McKendry, 2002a).



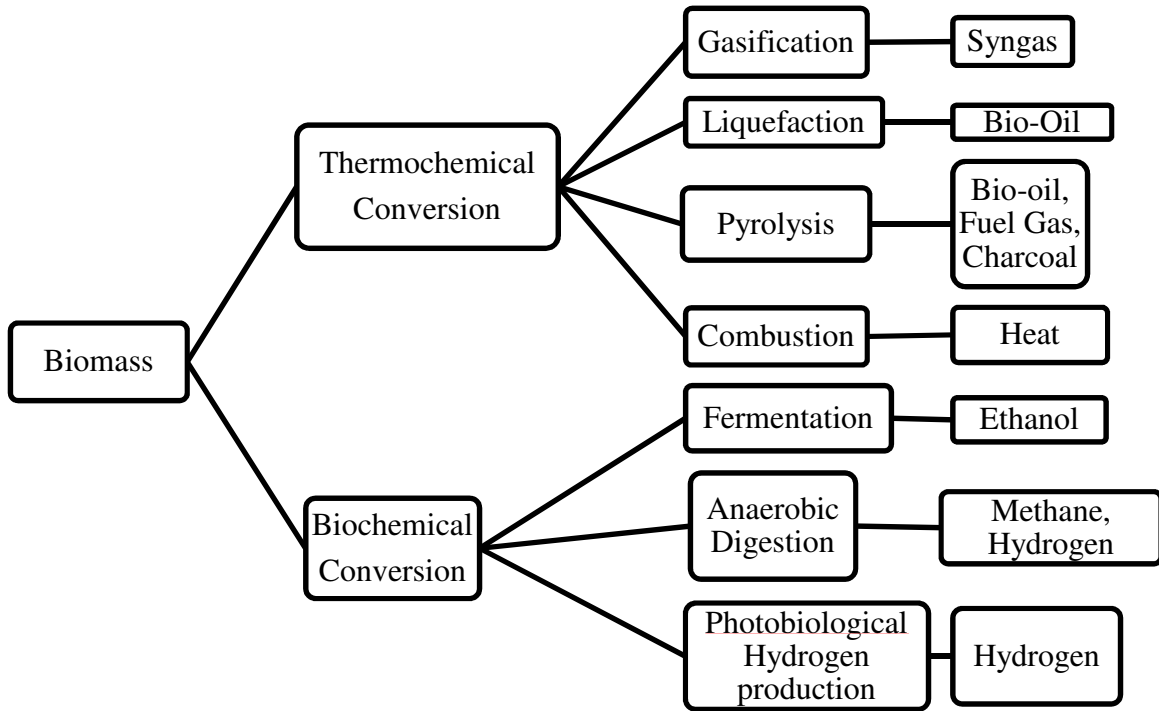


Figure 5 Potential biomass conversion processes. Adapted from (Tsukahara & Sawayama, 2005)

### Thermochemical Conversions

The main thermochemical conversions include gasification, liquefaction, pyrolysis, and combustion. The final energy products resulting from these processes are illustrated in figure 5.

### Gasification

Gasification is a process by where partial oxidation is achieved at high temperatures of a carbonaceous feedstock. The gasification occurs in three main steps, drying, pyrolysis, and gasification. This partial oxidation can be carried out using oxygen, air, or steam.

This feedstock can include biomass as well as coal. The process converts the feedstock into a gaseous energy carrier in two stages (Bridgwater, 1995). This gas is called syngas and mainly contains carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>). There are trace amounts of water vapor, nitrogen, ethane (McKendry, 2002c)

The gas produced can be used directly for fuel in gas turbines and gas engines. The syngas can also be used a feedstock to produce other chemicals such as methanol, hydrogen, dimethylether, and Fisher-Tropsch Diesel. Gasification of biomass has many possibilities to the production of transportation fuels (methanol, syngas, and hydrogen) as well as direct electricity conversions. Many of the technologies surrounding gasification are still in demonstration stages and show conversion efficiencies between 40-50% (McKendry, 2002b)

## Liquefaction

Hydrothermal liquefaction is a process to convert biomass to bio-oil with elevated temperatures (280-370°C) and high pressure (10-25 MPa) thermochemical process. The biomass is broken down into fragments in the presence of a solvent such as water. The small fragments are unstable and will re-polymerize into a variety of oily compounds. These can range from small particles with diverse boiling points and polarity to very large components. The final product is dependent on many factors: temperature, feedstock, heating rate, solvent, pressure, reducing gas, and residence times (Akhtar & Amin, 2011; Villadsen et al., 2012). The most important factor is temperature followed by types of solvent and biomass used. The secondary parameters are residence time, pressure, and reducing gas. Each type of biomass feed stock

needs to be optimized to have a final the desired product. Energy conversions efficiencies can very greatly and have been shown to be between 30-80% (Huang et al., 2013).

### Pyrolysis

Pyrolysis is the thermal decomposition of lignocellulose at high temperature (648-800K) in the absence of oxygen. This forms a gaseous product that then condenses. This process produces a complex mixture of oxygenated compounds by a series of parallel reactions that are too complicated to describe in a single reaction; dehydration, depolymerization, and C-C bond cleavage (Cai, Wu, Liu, & Huber, 2013; Wang, Male, & Wang, 2013). Pyrolysis forms high energy density bio-oil and char. Fast pyrolysis produces bio-oils as where slow pyrolysis produces solid fuel. This process has been shown to produce high yields with up to 80% by weight of dry feed. Important factors to consider with pyrolysis are that the biomass must be finely ground and there must be carefully controlled high temperatures followed by rapid cooling (Huber, Iborra, & Corma, 2006).

### Combustion

Combustion is the burning of biomass in air to produce hot gases. These hot gases can then be used for heat, electricity or mechanical power. The moisture content of the biomass must be less than 50%. This means that some biomass must be put through a drying process before combustion. Combustion of biomass is done on a very small scale, domestic heating, to large-

scale industrial plants. The net energy conversion range is from 20%-40% (Jenkins, Baxter, Miles, & Miles, 1998; McKendry, 2002b).

## Biochemical Conversions

Biochemical conversion of biomass utilizes the metabolism of microbes to extract the energy. Biochemical conversions include fermentation, anaerobic digestion, and photobiological hydrogen production.

### Fermentation

For fermentation the biomass must first be pretreated with mechanical process as to breakdown the size of the biomass. The biomass is then subjected to steam to destroy the cell structure. At this point the lignin is removed and can be used as feedstock for combustion. Enzymes break down the starch to sugars. The mixture is then fermented to ethanol through the use of yeast. The ethanol has to be purified by distillation.

Breaking down lignocellulosic biomass is more complicated due to the presence of longer chain polysaccharides. Enzymatic action is needed to break it down into monomeric and oligomeric sugars through enzymes. This is then hydrolyzed further into glucose. At this point yeast is able to ferment the sugars to ethanol (Chiaramonti et al., 2012; Hamelinck & Faaij, 2006; McKendry, 2002b; Modenbach & Nokes, 2013).

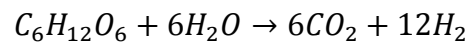
## Anaerobic Digestion

In anaerobic digestion, also called methanogenic fermentation, the biomass is directly converted to a mixture of CH<sub>4</sub> and CO<sub>2</sub> called biogas. In anaerobic digestion of biomass or other organic matter the absence of terminal electron acceptors produces CH<sub>4</sub> and CO<sub>2</sub>. This is accomplished through the use of heterogeneous microbial populations in an anaerobic environment. The anaerobic biodegradation occurs in four main stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Lakaniemi, Tuovinen, & Puhakka, 2013).

The resulting biogas can be used directly in gas turbines or, with CO<sub>2</sub> removal, as high quality natural gas. An advantage of this conversion process is that high moisture content of up to 90% can be used. This is currently being used for organic waste such as sewage and manure. There is between a 20-40% energy conversion to the biogas. If electricity is created the overall conversion is about 10-16% (McKendry, 2002b).

## Photobiological Hydrogen Production

Photobiological hydrogen (H<sub>2</sub>) production is a process by which microorganisms convert photon energy into H<sub>2</sub> (Posten & Schaub, 2009):



Two organisms shown to do this are green algae and cyanobacteria. The microorganisms accomplish this by a “coordinated action of oxygenic photosynthetic electron transport and the catalytic activity of a hydrogenase enzyme” (Ghirardi et al., 2007). The microorganisms absorb photon energy and conduct a water-splitting process without an

intermediate biomass stage. There are only two enzymes known to be capable of this: NiFe hydrogenases, found in green algae, and FeFe-hydrogenases, found in cyanobacteria.

Interestingly these two enzymes are completely phylogenetically distinct but perform the same catalytic reaction. Green algae have higher turnover rates than cyanobacteria. The wild type algae are able to convert solar energy in about a 10% efficiency to H<sub>2</sub> (Ghirardi, Dubini, Yu, & Maness, 2009; Ghirardi & Mohanty, 2010; Ghirardi et al., 2007). There are some studies being done with knockdown mutants that can produce H<sub>2</sub> in a 10 fold increase over wild type (Lin et al., 2013).

## Biofuels

Biofuels can be produced from a large variety of biomass. Many types of biofuels can be created ranging from liquid biofuels such as biodiesel and ethanol to gaseous and solid biofuels such as CH<sub>4</sub> and charcoal. On a very basic level there are essentially two steps to producing a biofuel: growth of biomass and subsequent processing, figure 6.

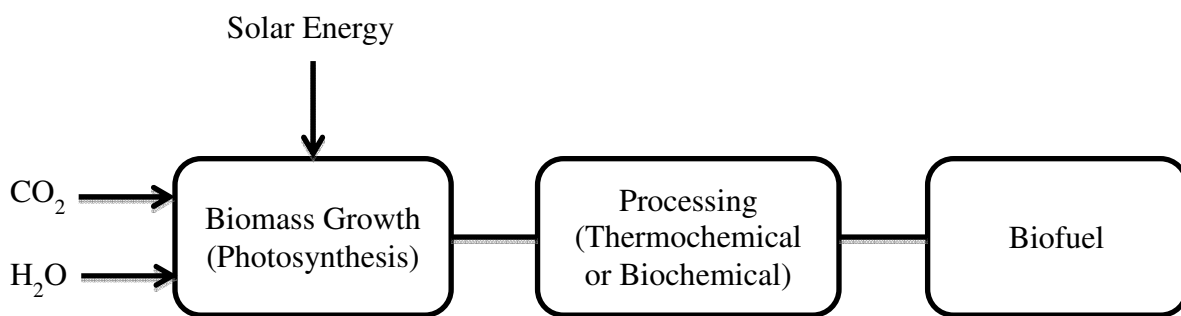


Figure 6 Basic biofuel production (Posten & Schaub, 2009)

First generation biofuels include ethanol from sugar/starch crops and plant oil-derived esters. These are liquids that have similar boiling points to gasoline and diesel fuels. Biodiesel defined by the National Biodiesel Board as “fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats” (“National Biodiesel Board: What is biodiesel? ,” 2013). Biodiesel can be used alone or in conjunction with diesel in a biodiesel/diesel blend (Posten & Schaub, 2009). Internationally these diesel/biodiesel blends are called B2, B5, B20, and B100 and are fuels with a concentration of 2%, 5%, 20%, and 100% of biodiesel. The most common being used today are blends between 5%-20% of volumetric proportions (Escobar et al., 2009). Biodiesel has a similar energy efficiency as petroleum diesel, lower CO<sub>2</sub> emissions, lower total particulate matter and carbon monoxide emissions, lower total water and solid waste. On a life cycle basis however there is higher water consumption in biodiesel (J. Sheehan, Cambreco, Duffield, Garboski, & Shapouri, 1998). Ethanol is the most widely used biofuel. It is an alcohol that is fermented from sugar and starch crops. Ethanol can also be blended with gasoline in any concentration. The most common concentrations are 10% and 85%, E10 and E85 respectively. Any concentration between 25% and 85% requires a dual fuel engine. 100% ethanol can also be used but require a different engine configuration.

There is a new generation of biofuels being developed called second-generation biofuels. These second generation biofuels include ethanol produced from lignocellulosic biomass and synthetic fuels produced from synthesis gas (Papalexandrou, Pilavachi, & Chatzimouratidis, 2008). Some of these fuels are gases at ambient conditions such as substitute natural gas (Syngas) and hydrogen (H<sub>2</sub>). A greater variety of biomass can be utilized as well as a higher proportion of the plant materials are some advantages of 2<sup>nd</sup> generation biofuels. Better engine configurations can also be utilized for improved combustion (Posten & Schaub, 2009). The first

commercial scale lignocellulosic biofuel facilities are expected to begin operations in 2013. By 2014, it is estimated that 215 million gallons of gasoline-equivalent energy products will be produced. Roughly half of this production will be hydrocarbon-based biofuels and half will be ethanol (Brown & Brown, 2013).

Biodiesel derived from oil plants such as algae and rapeseed are being called the third generation of biofuels. Figure 7 shows a breakdown of first and second and third-generation biofuels with their conversion routes from biomass to biofuels. Currently only ethanol and biodiesel are produced on an industrial scale (van der Laak, Raven, & Verbong, 2007). There are also large-scale conversions into biomethane. This could be used for transportation energy. There is also active research for biobutanol to be used as a supplement to gasoline and diesel (Antoni, Zverlov, & Schwarz, 2007).



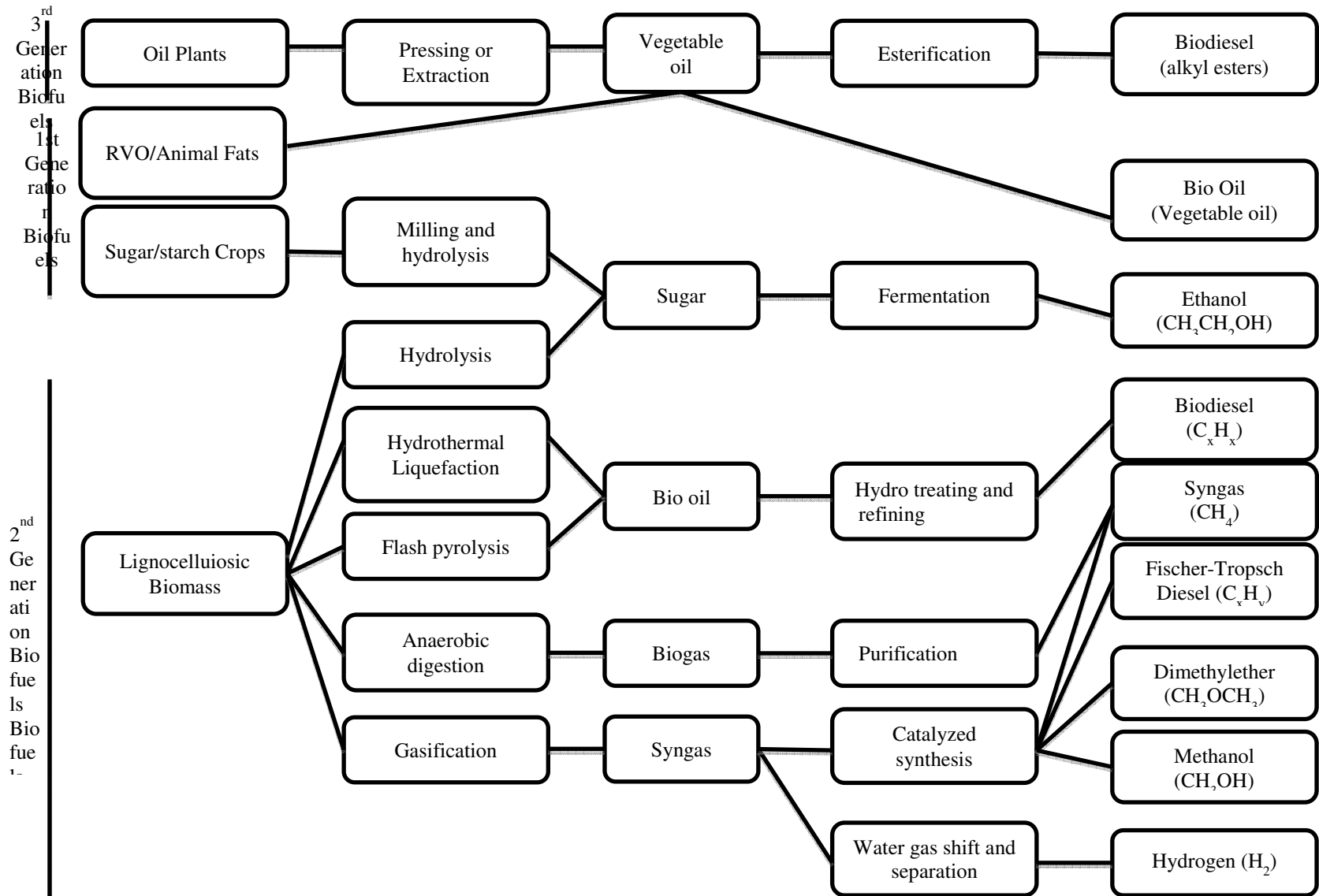


Figure 7 First and second and third generation biofuels with their conversion routes from biomass to biofuels. Adapted from (Agarwal, 2007; Hamelinck & Faaij, 2006)

## Disadvantages to Using Biomass

Although biomass has the potential to provide a renewable energy source for underdeveloped areas there are some concerns. One of these concerns is that the crops grown for energy could compete directly with food crops (Clarens, Resurreccion, White, & Colosi, 2010). Those that are most vulnerable to spikes in food prices that are brought on by a biofuel boom are in countries that already suffer food shortages. An ethanol boom in the United States in 2006 was a factor in the rise in corn prices worldwide. The United States provides 40% of the world's corn supply. In particular Mexico gets 80% of its corn from the United States and during 2006 the prices of corn doubled. For many of Mexico's poor, corn tortillas are the main source of calories and the rise in corn prices was devastating (Runge & Senauer, 2007). In some areas land is a scarce resource and devoting land for energy crops means less food crops are grown. As more corn is grown for ethanol there are less crops of wheat and soybeans. This means that not only prices for corn rise but also that of wheat and soybeans.

The environmental impact of energy crops is another important factor to consider when looking at biomass. Many crops of biomass are row crops that contribute to water pollution and soil erosion. Some of these crops require large amounts of fertilizer and pesticides. Careful analysis needs to be made for the total energy and labor needs to grow, harvest, transport and dry different biomass crops (Groom, Gray, & Townsend, 2008; Patzek & Pimentel, 2005; J. J. Sheehan, 2009).

## Biomass Energy from Algae

Algae have become increasingly attractive candidates for biomass. Algae are aquatic microscopic organisms and like terrestrial plants they assimilate CO<sub>2</sub> into biomass. Algae can be grown in freshwater or marine water with some species preferring brackish and some preferring hyper-saline conditions. An important benefit of algae over terrestrial crops is that much less land space is required. Algae can also be grown on land that is not suitable for other energy crops. Because algae isn't a main food staple and doesn't require vast amounts of land to grow, the food versus fuel problem is eliminated (Schenk et al., 2008; Tsukahara & Sawayama, 2005).

The types of algae range significantly from single-celled organisms (phytoplankton) to complex, differentiated forms such as seaweed. Some phytoplankton have flagella and are motile and some are non-motile. Algae produce long chain polysaccharides that are used to build their cell walls. This accounts for much of the carbon contained in algae. There are many different species of algae that produce more or less of certain compounds such as lipids and carbohydrates (Huerlimann, de Nys, & Heimann, 2010). Some species have been shown to produce up to 70% oil by wet weight (J. Singh & Cu, 2010).

Like terrestrial plants, algae require solar energy, CO<sub>2</sub> and H<sub>2</sub>O. Algae growth also requires the nutrients nitrogen and phosphorus. One advantage with algae over terrestrial crops is that when algae are grown in closed photobioreactors, only the amounts of the nutrients needed are used. This prevents the loss to the environment as with row crops (Posten & Schaub, 2009). Not only do algae use less nutrients they also use less water than many common terrestrial energy crops. When compared by water usage per energy (l/MJ), corn and rapeseed used significantly more water than algae (Dismukes, Carrieri, Bennette, Ananyev, & Posewitz, 2008). Algae can also use seawater and wastewater while terrestrial crops require fresh (Amin, 2009).

Algae are efficient organisms for converting solar energy into biomass (Schenk et al., 2008). They are the highest producers of oil among the oil plants and convert 5% of solar energy into biomass. If the desired energy product is biodiesel a species of algae can be selected that will optimize the production. Algae can also be grown all year as opposed to many terrestrial plants and thus have a near continuous harvest stream. Algae have the potential to produce many types of energy including methane, biodiesel, hydrogen and ethanol (figure 8) (Johnson & Wen, 2009; Roncarati, Meluzzi, Acciarri, Tallarico, & Melotti, 2004).

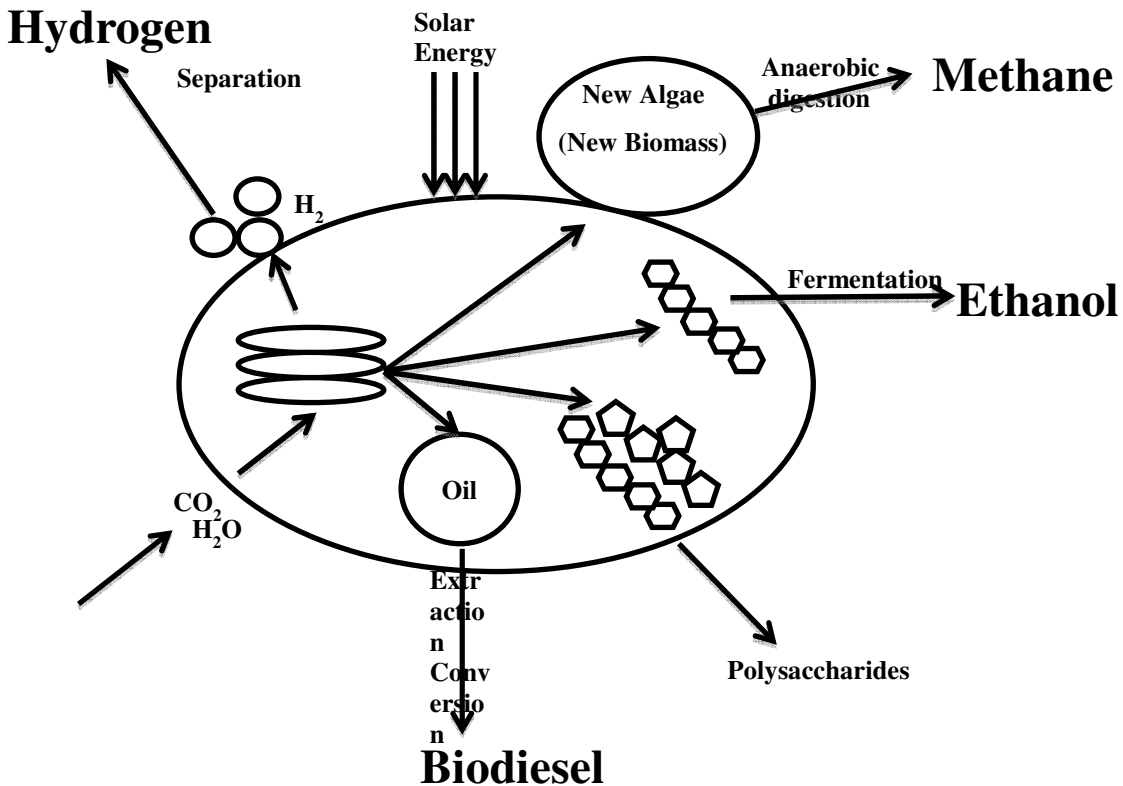


Figure 8 Energy products from algae. Adapted from (Posten & Schaub, 2009)

The two main ways that algae are grown are open ponds or closed photobioreactors. An open pond is simply an open tank or natural pond. The highest productivity for open ponds is found using an elliptical shape that is mechanically mixed called a raceway (A. Singh, Nigam, & Murphy, 2011). In closed photobioreactors higher productivity is accomplished but more energy is used to maintain the system (Cornet & Dussap, 2009). Work is being done to develop integrated photobioreactors next to power plants that can utilize the CO<sub>2</sub> emissions and waste heat (Patil et al., 2008). Some studies have used photobioreactors with no added heat at mid-temperature latitudes and achieved high cell densities (Hulatt & Thomas, 2011). While this is very promising for integrated biofuel production, rural and underdeveloped areas would benefit from open ponds that require less energy and effort to maintain.

Algae have the potential to produce many types of energy including methane, biodiesel, hydrogen and ethanol (figure 8). While biodiesel derived from algae has the potential to completely displace petroleum derived liquid fuels, there is still much work to be done. Algae biology needs to be optimized through genetic engineering (Chisti, 2007; Chiu et al., 2009). Biodiesel also benefits from the closed photobioreactors that aren't feasible in undeveloped areas.

### Algae Use in a Diesel Engine

Instead of processing the algae into one of previously discussed energy products, a way to directly use the algae without further processing to produce electricity would be greatly desirable. One way in which this might be accomplished is to directly use algae as an alternative fuel in a stationary diesel engine generator.

A diesel engine is an internal combustion engine that uses heat produced by the compression of air to ignite fuel. The diesel engine was first designed by Dr. Rudolph Diesel in the late 1800's to use coal dust (Diesel, Aug 9, 1898, Jul 16, 1895). Dr. Rudolph's first demonstration diesel engine was completed in 1897 and ran off peanut oil (*The Diesel Engine*, 1913). The first diesel engine to be placed under regular operating conditions was built in 1898 in St. Louis, Missouri by Mr. Adolphus Busch (*The Diesel Engine*, 1913). Although petroleum based diesel has been the main fuel used for diesel engines, vegetable oils, peanut oil, animal fats and rapeseed oil have all been used in diesel engines (Kleinova, Vailing, Labaj, Mikulec, & Cvengros, 2011; Kumar, Bellettre, & Tazerout, 2009; Qi, Bae, Feng, Jia, & Bian, 2013). Alternative fuels for diesel engines is an active area of research with biodiesel being the most studied (Srivastava & Prasad, 2000).

A patent published in 1989 describes a way to use a coal slurry with equal parts coal dust and water to run a diesel engine. This method uses a "vortex swirl nozzle" to inject the slurry into the combustion chamber. This vortex nozzle has an opening that is larger than the conventional nozzle and eliminates the clogging associated with coal dust use in diesel engines (Holmes, Sep 5, 1989).

The first step to discover if directly using algae as an alternative fuel in a diesel engine might be plausible is to find the heat of combustion for algae and compare that to diesel fuel.

## CHAPTER III

### HEAT OF COMBUSTION FOR ALGAE

#### Experimental procedure

##### Apparatus

The goal of this study is to determine the heat of combustion for the specific strain of algae. To accomplish this a bomb calorimeter from Parr Instrument Company was used, Oxygen Bomb Calorimeter 1341 (Parr Instrument, September 9th, 2008) and Oxygen Combustion Bomb 1108 (Parr Instrument, November 27th, 2012). A bomb calorimeter is a metal reaction chamber that is submerged in a water bath of known volume. This water bath is insulated to prevent heat transfer to the outside environment thus creating an adiabatic system. Inside this water bath is a reaction chamber of constant volume known as a “bomb.” The bomb is a very rigid structure that can withstand large expansion pressure while not significantly changing its volume. The bomb is pressurized with oxygen, and the sample is ignited through a fuse wire. The combustion reaction increases the temperature inside the bomb, which transfers the heat to the external water bath. A thermometer is placed in the water and the rise in temperature is monitored, figure 9. This temperature rise is used to calculate the energy released.

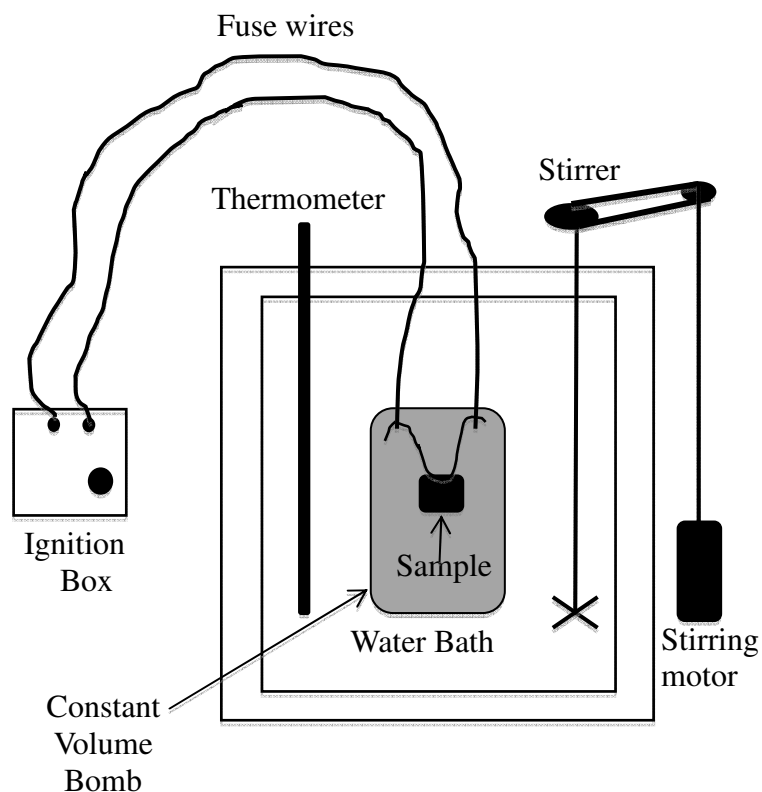


Figure 9 Schematic of bomb calorimeter used

### Charging the Calorimeter

The following procedure was obtained and summarized according to the Parr 1341(Parr Instrument, September 9th, 2008) and 1108 Operating Manual (Parr Instrument, November 27th, 2012). The bomb was opened and placed on the support stand. 10 cm of the fuse wire was attached between the two electrodes. This is done by raising the caps over the electrodes and threading the wire through the eyelet. The cap is then pushed down locking the wire in place. The fuse capsule with a weighted sample is placed in the electrode loop. The wire is then bent down and placed so that it is just touching the sample, figure 10. The fuel capsule is



then slightly bent so the flame will not directly interfere with the electrode.

Since combustion takes place in an atmosphere of almost pure oxygen at high temperature and pressure, several reactions occur that would not if the same material were burned under normal atmospheric conditions. Oxides of nitrogen are formed from nitrogen present in the oxygen mixture. 1.0 mL of deionized water is placed inside the bomb with a pipet to act as a sequestering agent for these compounds. The bomb head is then carefully moved to the bomb cylinder and placed straight down without twisting. Care is made to not disturb the sample. The lid is then hand tightened and the outlet valve is closed.

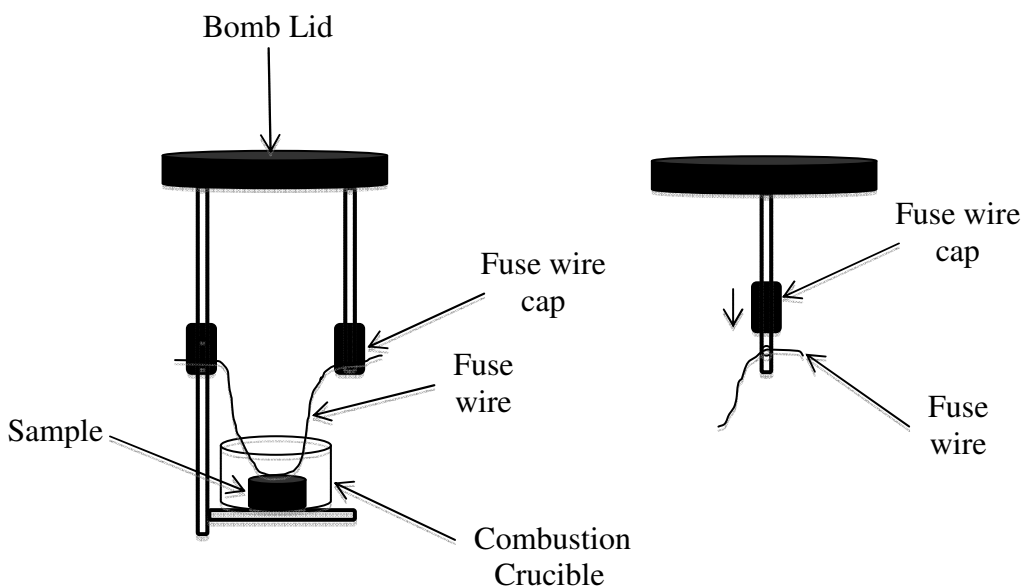


Figure 10 Schematic of sample support stand and ignition wire

At this point the bomb is charged with oxygen. This is done with 1825 oxygen filling connection. This is a slip connector that slides over the gas inlet fitting on the bomb lid. The

outlet valve on the lid is now closed. The filling connection is now slowly opened until the pressure rises to between 30-40 atm. The bomb vessel inlet check valve automatically closes when the oxygen supply valve is closed. The bomb is now properly charged and ready.

### Firing the Calorimeter

After the bomb has been charged with oxygen, 2000 grams of water 1°C below room temperature is then added to the bucket. The handle is used to lower the bomb into the water being careful to not remove any water from the bucket. The two ignition lead wires are then carefully pushed into the terminal sockets while also avoiding letting fingers remove any water from the bucket. They are arranged away from the stirrer shaft so they do not become tangled in the stirring mechanism. The bomb is then carefully examined for leaks. If any leaks are observed then the bomb must not be fired and the procedure must be started over.

The cover is placed over the bucket and the drive belt is placed over the pulleys. The motor is now started and the digital thermometer is turned on. The lead wires of the calorimeter are connected to the 10 cm binding post and the common terminal of the ignition unit. The stirrer is set to run for 5 minutes before the measured run is completed. At this point the temperatures are read and recorded at one-minute intervals for 5 minutes. At the start of the 6th minute, the bomb is fired by pressing the ignition button and holding it down until the indicator light goes out. This is usually accomplished in about 0.5 seconds. Don't hold the ignition for more than 5 seconds. Head, hands, and any body part should not be over the bomb during firing and should be kept clear for 30 seconds. After initial ignition, temperatures are recorded at 45, 60, 75, 90, and 105 seconds after firing. The 60% point is interpolated between these points. The temperature is then recorded every minute until the temperature has not changed for 5 minutes.

## Analysis of Combustion

After this time the combustion products were recovered. The motor is stopped, the belt is lifted, and the cover is removed. The bomb is carefully lifted out. The residual gas pressure must be released by slowly opening the release valve. After all the pressure is released the bomb head is placed in the support stand. The inside of the bomb must be examined for evidence of incomplete combustion. If this is discovered then the test will have to be discarded. The bomb is then washed with distilled water and the washings are collected in a beaker.

The bomb washings are titrated in a 0.0709N sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) solution using methyl red indicator. When doing the titrations it is assumed that all the acid formed is nitric acid ( $\text{HNO}_3$ ) and that the heat of formation of 0.1N  $\text{HNO}_3$  is 14.1 Kcal per mol. The corrections in calories for the heat of combustion for nitric acid will be denoted  $e_1$  and  $v$  is used to denote volume of  $\text{Na}_2\text{CO}_3$  used:

$$e_1 = v_{\text{Na}_2\text{CO}_3} \times 1\text{cal/ml}$$

(1)

The unburned pieces are also removed from the electrodes and measured. The wire used for the ignition is not entirely used up in the combustion. The portion of wire that is consumed contributes to the heat of combustion. There is also heat generated through the wire by resistance during the electric firing. The amount of wire that is consumed varies from test to test. To account for this the amount of unburned wire is subtracted from the 10cm of wire initially used in the bomb. For these experiments Parr 45C10 wire that is utilized that has a pre-determined energy per length value. For this wire the heat of combustion is 2.3 calories per cm. To solve for this correction in calories for the heat of combustion of the fuse wire is denoted as

$e_2$  and  $l$  is used to denote length of fuse wire used:

$$e_2 = l_{fuse\ wire} \times 2.3cal/cm \quad (2)$$

### Assemble and Plot the Data

The temperature and time data for each run (example shown in table 1) should be plotted as shown in figure 11. Point 'i' denotes initial measurement, point 'a' denotes time of firing, point 'b' denotes when the temperature reaches 60% of total rise, 'c' denotes the time at the beginning of a period in which the rate of change has become constant, and 'd' denotes final point of measurement. The initial and final temperatures are not stable and this change in temperature must be accounted for in calculating the change in temperature ( $\Delta T$ ) for the reaction. For this reason solving for  $\Delta T$  by the following the approach cannot be used:

$$\Delta T = T_c - T_a \quad (3)$$

By assuming a linear baseline the rates of change can be found by using a difference approximation:

$$r_1 \approx \frac{T_a - T_i}{a - i} \text{ and } r_2 \approx \frac{T_d - T_c}{d - c} \quad (4)$$

The  $r_1$  is the rate expressed in  $^{\circ}C$  per minutes of the temperature rising during the 5 minutes before the firing and  $r_2$  is the rate expressed in  $^{\circ}C$  per minutes of the temperature rising after the rise period between point b and c. Thus you can solve for the net corrected temperature rise ( $\Delta T$ ):

$$\Delta T = (T_c - r_2(c - b)) - (T_a - r_1(b - a)) = T_c - T_a - r_1(b - a) - r_2(c - b) \quad (5)$$

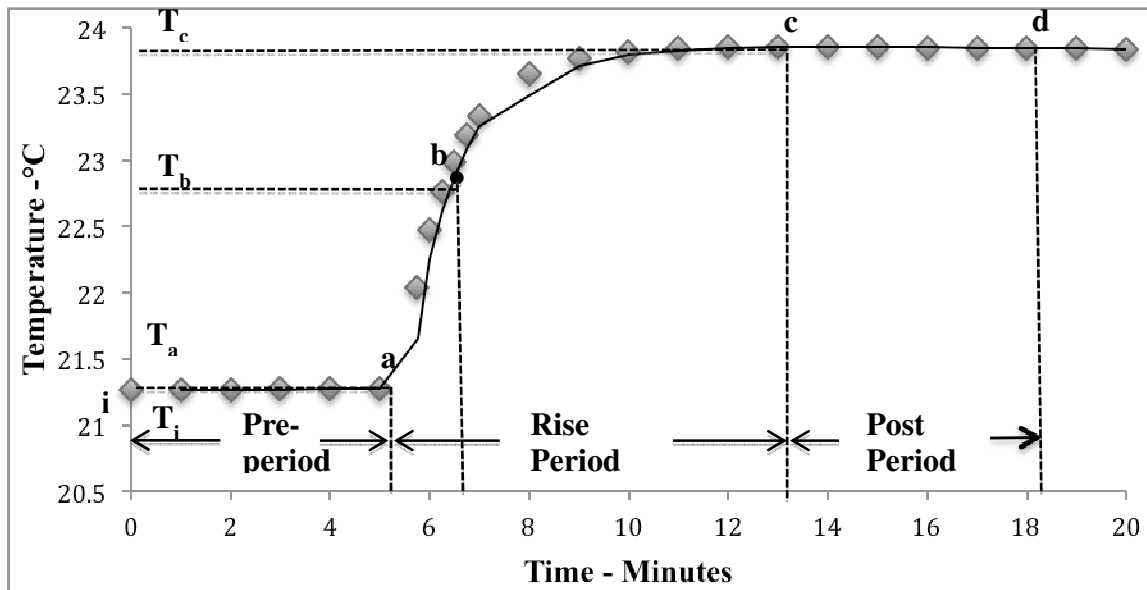


Figure 11 Typical temperature versus time plot for bomb calorimeter created using benzoic acid. The positions of  $T_i$ ,  $T_a$ ,  $T_b$ ,  $i$ ,  $a$ ,  $b$ ,  $c$  and  $d$  are shown. Definitions for these points are given in the text

Table 1 Typical temperature and time data for a bomb calorimeter using a benzoic acid pellet. The positions of i, a, b, c and d are shown. Definitions for these points are given in the text

<b>Time</b>	<b>Temp</b>	
<b>x (min)</b>	<b>y (°C)</b>	
0	21.262	i
1	21.266	
2	21.269	
3	21.271	
4	21.273	
5	21.275	a (Fired Bomb)
5.75	22.037	
6	22.473	
6.25	22.767	b is interpolated
6.5	22.981	
6.75	23.183	
7	23.333	
8	23.649	
9	23.766	
10	23.818	
11	23.842	
12	23.852	
13	23.855	c
14	23.854	
15	23.852	
16	23.849	
17	23.846	
18	23.843	d
19	23.84	
20	23.837	

## Standardization of Bomb Calorimeter

There are slight differences in every bomb calorimeter and so each must be “standardized” before experiments can begin. This is done with a standard sample from which the energy equivalence or effective heat capacity of the system can be determined. Standardizing the system gives the energy equivalence factor ( $W$ ), which represents that amount of energy required to raise the temperature of the specific calorimeter one degree Celsius. This can be done with any standard sample but it is common to do this with benzoic acid. The following procedure is summarized from instruction manual (Parr Instrument, September 9th, 2008)

Benzoic acid must always be pressed into pellets before it is burned in the bomb calorimeter to avoid damage from rapid combustion of loose powder. In these experiments pre-pressed benzoic acids provided from Parr Instrument Company were used. The heat of combustion ( $H_g$ ) for the standard benzoic acid in these samples is 6318 cal/gram. The pellets must be between 0.90-1.25 grams. The benzoic acid pellet mass is carefully taken and recorded. The procedure for the standardization test is the same described previously for testing a fuel sample. The corrected temperature rise ( $\Delta T$ ) is calculated from data using equation (5). Using the mass of the benzoic acid in grams ( $m$ ),  $\Delta T$ , the heat of combustion for benzoic acid ( $H$ ), the correction for heat of formation of nitric acid in calories ( $e_1$ ), the correction for the heat of combustion for the fuse wire ( $e_2$ ), the following equation can be used to solve the energy equivalence factor ( $W$ ):

$$W = \frac{Hm + e_1 + e_2}{\Delta T} \quad (6)$$

The energy equivalence factor describes the heat capacity of the system in how much calories is needed to raise the temperature 1°C.

Once the bomb calorimeter is standardized the procedure can be repeated for desired sample and used to find the  $\Delta H$ :

$$H_g = \frac{\Delta TW - e_1 - e_2}{m} \quad (7)$$

The bomb calorimeter was calibrated with three trials using benzoic acid. The percent error was calculated using excel by implementing the methods described in, Statistical Treatment of Experimental Data, (Young, 1962). A sample calculation can be seen in the appendix E.

### Algae Preparation

Green saltwater algae (nannochloropsis) that were used for these experiments were purchased from Carolina Biologicals. The algae were grown in saltwater media at room temperature. The algae were grown in a 20-gallon open aquarium and exposed to the ambient light in the laboratory. The algae were treated to a 120 V, 60 Hz, 1.49 A light bulb for 4 hours every 4 hours.

The algae were collected from the tank using a sterilized pipet. The algae were washed twice with distilled water through subsequent centrifugation. The washed algae were placed in a crucible and desiccated at 105°C. The desiccated algae were then ground into a fine powder. Many attempts to combust algae alone were unsuccessful. If the algae were placed in crucible as a powder or pellet no identifiable combustion was observed. Placing some cotton in the crucible with the algae allowed for partial combustion. To solve this problem the algae were mixed with



coal dust. When this was done all the algae combusted. Because coal dust was used as an accelerant the heat of combustion for the coal was first determined before the algae was determined. Five samples of coal dust and five sample of coal dust /algae sample were combusted. The percent error was calculated using excel by the methods described in Statistical Treatment of Experimental Data (Young, 1962).

### Experimental Results

The heat capacity of the calorimeter has a value  $2434.93 \pm 2.7$  cal/°C and was calculated using equation (6). Three experimental trials were performed and the time/temperature data can be seen in the appendix under A-1 and A-4. The heat of combustion for the coal dust was found to be  $7010.36 \pm 56.2$  cal/g using equation (7). The time/temperature data can be seen in the appendix under Tables A-2 and A-5 .The heat of combustion for the algae was found to be  $4471.2 \pm 95.1$  cal/g (table 2). The time/temperature data can be seen in the appendix under A-3.

### Discussion

The caloric value for all plant species lies somewhere between 4000-5000 cal/g (McKendry, 2002a). The algae tested in this experiment were found to have a caloric value  $4471.2 \pm 95.1$  cal/g. Diesel produced from petroleum has a density of 0.84 g/ml and an energy content of 35 MJ/L (Posten & Schaub, 2009). This is 9959 cal/g and over twice the amount of energy per gram than the algae tested.

When the diesel engine was first invented it was designed to use coal dust (Diesel, Aug 9, 1898, Jul 16, 1895). The desiccated algae and coal dust had similar consistencies and it is

conceivable that directly using the algae might be possible. In these experiments coal dust was about a third more energy dense than algae. Even though the heat of combustion for algae and coal were closer than that of diesel fuel, the ignition point of algae was significantly higher. Algae alone in the bomb calorimeter would not combust. A system described in patent 4,862,837 utilizes a coal dust and water slurry that might be used with algae (Holmes, Sep 5, 1989). A system like this would also be advantageous because the algae would not have to be desiccated. A test engine was built by Adiabatics Inc. of Columbus Indiana in 1991 and uses this design (Badgley & Doup, May 1991). A single-cylinder diesel test engine was built to optimize the coal/water slurry injection system. One concern with using a coal/water slurry is that tremendous wear is detected in the injection systems. This test engine used an electronically controlled, hydraulically actuated coal/water slurry injection system that alleviated this wear on the nozzle spray orifice. This diesel engine used 100 % coal/water slurry without an ignition assist and achieved 1,800 rpm. This was accomplished with low injection pressures of 13.8-20.7 MPa (2000-3000 psi). This test engine also employed a thermal ignition combustion system (Kamo, Kakwam, EdgarsValdmanis, & Melvins E. Woods, Apr.19,1988). The authors note that coal particles were found in three parts of the engine: exhaust valve rotators and springs, cylinder liners, and oil. During their testing the particles did not cause problems but it is conceivable that after long runs with a commercial engine this might become a problem. They also encountered nozzle orifice and cylinder head cracking. During the testing process they introduced some modifications that alleviated these problems. A report published in 1995 under the sponsorship of the Department of Energy, Cooper-Bessemer and Arthur D. Little Inc. developed a full scale (6 cylinder, 1800 kW) Cooper-Bessemer Model LS engine (Cooper-Bessemer & Arthur D. Little, 1995). This engine also ran off of a coal dust/water slurry. Two hundred hours of full-

scale engine testing were done. Major achievements with this engine were durable injection nozzles, integrated emissions control system, and low cost clean coal slurry formulations. Using a system such as this for an algae/water slurry or an algae/coal/water slurry might be possible.

Another option would be to mix the algae with diesel fuel. One study mixed diesel fuel with vegetable oils, methanol, ethanol, and biodiesel and found that “properly blended fuels yield comparable engine performance and emission characteristics, while their use requires no modification in diesel engines” (Karabektas, Ergen, & Hosoz, 2013). Although algae are very different than the previously listed additives it is conceivable that algae and diesel fuel could be mixed. This doesn't alleviate the problems associated with using fossil fuels but it would be better than completely relying on fossil fuels. In the beginning a mixture of 80% diesel and 20% algae might be used. As time goes by and the price of diesel continues to rise, the percentage of algae will probably be raised as more engine modifications technologies are developed.

Using alternative fuels for diesel engines such as vegetable oils and animal fats have been shown to cause injector coking, piston ring sticking, and severe engine deposits (Srivastava & Prasad, 2000). Engine modifications have shown to alleviate these problems and it is conceivable that combustion process and other modifications might make using algae directly feasible. Future studies would include using a test engine to see if algae could be directly used. Mixtures of algae with diesel fuel and coal dust should also be performed to discover if certain blends would require no modifications.

Table 2 Heat of Combustion for Algae

Experimental Trial	Hg cal/gram (coal-algae)	Total grams coal	Total grams algae	Total calories from coal	Total Calories from Algae	Error ±	Algae Hg (cal/gram)	Error ±
Algae/Coal Dust #1	5692.7	0.400	0.455	2802.7	2061.7	±22.5	4534.2	±49.4
Algae/Coal Dust #2	5547.2	0.431	0.572	3023.6	2543.6	±24.3	4444.5	±42.4
Algae/Coal Dust #3	5740.3	0.501	0.502	3515.0	2244.3	±28.2	4471.6	±56.2
Algae/Coal Dust #4	5698.9	0.500	0.507	3508.0	2230.8	±28.1	4403.4	±55.5
Algae/Coal Dust #5	5754.4	0.501	0.503	3515.0	2264.1	±28.2	4502.2	±56.1
Average							4471.2	±95.1

## Conclusion

There are nearly 1.6 billion people living without any access to electricity. Many of these people live in rural areas without any access any modern energy. Fossil fuels can bring in the much needed electricity but they bring with them a number of problems. Fossil fuels are responsible for much pollution and green house gas emissions. Many areas do not have their own fossil fuel resources and have to have them brought in. This leaves them vulnerable to inevitable price hikes and supply disruptions. In an ideal situation providing an underdeveloped area its first access to electricity through a renewable resource will alleviate these issues.

There are many options for renewable energy but a particularly attractive one is biomass. Biomass can provide a clean and reliable source. Almost every country has access to some sort of biomass. In choosing a biomass the criterion for selection should be what type of biomass is locally available, what type of energy is needed, and the energy conversion rates. Algae are a good candidate for many areas for a number of reasons:

- Very little land use
- Able to use non-arable land
- Can adapt to many environments
- Very efficient solar energy collectors
- Near-continuous harvest stream
- Many conversion technologies are simpler than for lignocellulosic biomass

Finding a way to use algae to provide electricity for underdeveloped areas is a very exciting prospect. Although algae can be used to create biodiesel, methane, ethanol, and hydrogen these technologies are complicated and are still in the demonstration phases. A simple

approach would be to use the algae directly as an alternative fuel in a diesel engine. In this study a specific strain of algae was grown, collected, and desiccated before using a bomb calorimeter to calculate the heat of combustion. When this was done the algae was found to have  $4471.2 \pm 95.1$  cal/g. While this is under half the energy density of diesel fuel further research needs to be done to see if engine modifications could be done to make this feasible.

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APPENDIX A

TABLE A.1 BENZOIC ACID TEMPERATURES AND TIME MEASUREMENTS

Substance	Benzoic Acid #1	Benzoic Acid #2	Benzoic Acid #3
Time(min)	Temp (°C)	Temp (°C)	Temp (°C)
0	21.262	19.855	20.171
1	21.266	19.862	20.177
2	21.269	19.868	20.181
3	21.271	19.872	20.185
4	21.273	19.877	20.189
5	21.275	19.881	20.195
5.75	22.037	20.595	20.888
6	22.473	20.943	21.271
6.25	22.767	21.312	21.61
6.5	22.981	21.53	21.821
6.75	23.183	21.723	22.051
7	23.333	21.931	22.202
8	23.649	22.199	22.535
9	23.766	22.358	22.679
10	23.818	22.423	22.744
11	23.842	22.452	23
12	23.852	22.467	22.783
13	23.855	22.473	22.789
14	23.854	22.476	22.79
15	23.852	22.477	22.789
16	23.849	22.477	22.789
17	23.846	22.476	22.788
18	23.843	22.475	22.786
19	23.84	22.475	22.784
20	23.837	22.473	22.782

APPENDIX B

TABLE A.2 COAL DUST TEMPERATURES AND TIME MEASUREMENTS



Substance	Coal #1	Coal #2	Coal #3	Coal #4	Coal #5
Time(min)	Temp (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Temp (°C)
0	21.167	21.737	21.14	21.491	20.51
1	21.177	21.736	21.142	21.493	20.513
2	21.185	21.737	21.144	21.495	20.515
3	21.191	21.738	21.146	21.496	20.518
4	21.196	21.738	21.148	21.497	20.521
5	21.197	21.739	21.149	21.498	20.523
5.75	21.793	22.437	21.933	22.252	21.362
6	22.222	22.783	22.375	22.564	21.8
6.25	22.458	22.992	22.66	22.844	22.156
6.5	22.743	23.257	22.87	23.0492	22.388
6.75	22.895	23.369	23.059	23.195	22.612
7	23.055	23.535	23.203	23.328	22.786
8	23.345	23.833	23.535	23.623	23.175
9	23.476	23.965	23.66	23.736	23.336
10	23.538	24.02	23.715	23.784	23.403
11	23.562	24.047	23.743	23.807	23.433
12	23.571	24.056	23.75	23.816	23.445
13	23.573	24.058	23.753	23.818	23.449
14	23.573	24.058	23.751	23.817	23.449
15	23.571	24.056	23.749	23.815	23.447
16	23.568	24.052	23.746	23.812	23.444
17	23.564	24.048	23.742	23.808	23.44
18	23.56	24.044	23.738	23.805	23.437
19	23.558	24.039	23.734	23.801	23.433
20	23.551	24.036	23.75	23.797	23.43

APPENDIX C

TABLE A.3 ALGAE COAL DUST TEMPERATURES AND TIME MEASUREMENTS

Substance	Coal-Algae #1	Coal-Algae #2	Coal-Algae #3	Coal-Algae #4	Coal-Algae #5
Time(min)	Temp (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Temp (°C)
0	21.584	20.273	21.8	20.415	21.347
1	21.589	20.278	21.803	20.422	21.349
2	21.585	20.283	21.806	20.429	21.352
3	21.6	20.287	21.808	20.435	21.354
4	21.602	20.292	21.81	20.44	21.356
5	21.607	20.296	21.812	20.445	21.358
5.75	22.241	21.004	22.467	21.235	21.924
6	22.55	21.344	22.862	21.574	22.356
6.25	22.714	21.567	23.156	21.835	22.651
6.5	22.891	21.778	23.321	22.026	22.931
6.75	23.049	21.964	23.509	22.174	23.083
7	23.156	22.099	23.686	22.329	23.23
8	23.428	22.396	23.976	22.613	23.544
9	23.538	22.52	24.104	22.744	23.663
10	23.586	22.574	24.16	22.789	23.717
11	23.609	22.602	24.183	22.826	23.739
12	23.617	22.616	24.192	22.837	23.747
13	23.619	22.62	24.195	22.843	23.749
14	23.618	22.623	24.194	22.846	23.75
15	23.615	22.624	24.193	22.846	23.749
16	23.612	22.625	24.191	22.847	23.747
17	23.608	22.625	24.188	22.847	23.744
18	23.604	22.625	24.186	22.847	23.741
19	23.6	22.625	24.182	22.847	23.737
20	23.596	22.625	24.179	22.846	23.7354
20	23.596	22.625	24.179	22.846	23.7354

APPENDIX D

TABLE A.4 STANDARDIZATION OF BOMB CALORIMETER USING BENZOIC ACID

Experimental Trial	W (cal/ °C)
Benzoic Acid #1	2432.0
Benzoic Acid #2	2435.6
Benzoic Acid #3	2437.2
Average	2434.9 ± 2.7

APPENDIX E

TABLE A.5 HEAT OF COMBUSTION FOR COAL DUST

Experimental Trial	Hg (cal/°gram)
Coal Dust #1	6992.80
Coal Dust #2	6969.47
Coal Dust #3	7086.20
Coal Dust #4	6999.10
Coal Dust #5	7004.23
Average	7010.36 ± 56.2

APPENDIX F  
SAMPLE CALCULATION



The National Institute of Standards (NIST) have shown that the time when the temperature has risen by 60% of the difference between  $T_a$  and  $T_c$  to be the most accurate time to use for your calculations (Salzberg, 1966).

From the example shown in figure 11 and table 1, a benzoic acid pellet of 0.9934 grams was combusted. 8.4 cm of fuse wire was used up in the experiment and 9.65 mls of a 0.0709N  $\text{Na}_2\text{CO}_3$  solution was used for titration. The temperature rise at 60% of the total temperature rise was 2.580 °C and was solved using equation (5). The temperature at 60% of total rise ( $T_b$ ) is then calculated to be 22.823°C. Using the temperatures recorded at 45, 60, 75, 90, and 105 seconds after firing the time at 60% of total rise (b) is then calculated using linear interpolation. Linear interpolation between two known points is solved by:

$$\frac{y - y_0}{x - x_0} = \frac{y_1 - y_0}{x_1 - x_0}$$

Solving for the unknown y yields:

$$y = y_0 + (y_1 - y_0) \frac{x - x_0}{x_1 - x_0}$$

Substituting the values for the example shown in figure 11 and table 1:

$$b = 6.25 \text{ min} + (22.823^\circ\text{C} - 22.767^\circ\text{C}) \frac{6.5 \text{ min} - 6.25 \text{ min}}{22.981^\circ\text{C} - 22.767^\circ\text{C}} = 6.316 \text{ min}$$

Using the data shown from the example shown in figure 11 and table 1, W was calculated as follows:

$$H = 6318 \text{ cal/gram}$$

$$m = 0.9934 \text{ g}$$

$$e_1 = (9.65 \text{ ml})(1 \text{ cal/ml}) = 9.65 \text{ cal}$$

$$e_3 = (8.4 \text{ cm})(2.3 \text{ cal/cm}) = 19.32 \text{ cal}$$

$$\Delta T = 23.855^{\circ}\text{C} - 21.275^{\circ}\text{C} - \frac{0.0026^{\circ}\text{C}}{\text{min}}(6.315\text{min} - 5\text{min}) \\ - \frac{0.0024^{\circ}\text{C}}{\text{min}}(13\text{min} - 6.315\text{min}) = 2.593^{\circ}\text{C}$$

Substituting this in equation 6 yields:

$$W = \frac{6318 \frac{\text{cal}}{\text{g}}(0.9934\text{g}) + 8.65\text{cal} + 19.32\text{cal}}{2.593^{\circ}\text{C}} = 2432.005 \text{ cal}/^{\circ}\text{C}$$

## VITA

Cassia Davis is a cross-disciplined trained engineer with experiences in business and technology development. She started her academic career in chemistry earning both an undergraduate degree in biochemistry from Lee University and a Cell and Developmental Biology graduate degree from Vanderbilt University. She has always enjoyed engineering and worked as an engineering assistant and drafter while in college assisting in the various roles of design, drafting, and overseeing of manufacturing of equipment centers, operator centers, and electrical enclosures. Realizing her true passion lay with chemical engineering, she went to The University of Tennessee at Chattanooga to earn a master's in chemical engineering.

While studying for her masters in chemical engineering at UTC, Cassia worked at The Enterprise Center. There Cassia served as a technical and science liaison, reviewing patents and technology from federally funded laboratories such as Oak Ridge National Laboratories, Marshall Space Flight Center, and B&W Y12. The research she provided supported companies and entrepreneurs with technology development and innovation. The Enterprise Center deals with many different types of technology but focuses on alternative energy and transportation development.