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Biofuels Summary

An Interactive Qualifying Project Report

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1. Abstract:

Current stores of fossil fuels are being depleted rapidly. In order to keep up with increasing energy demands, alternative methods of producing commercially viable fuels must be established. Biologically derived fuels (biofuels) allow for sustainable fuel production. There is a diverse assortment of feedstocks and processes available for biofuel production. Processes of major industrial importance include esterification of animal fats, normal vegetable oils and oil from algal biomass. This report summarizes each process focusing on the relative energy and resource usage. It also considers the socioeconomic and technological issues associated with each of these methods of biofuel production.

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4. Introduction

In 1983 the United Nations formed the Brundtland Commission to deal with increasing concern "about the accelerating deterioration of the human environment and natural resources and the consequences of that deterioration for economic and social development."[1] In response to this task they produced a short report that defined and stated in general terms how sustainable development should be achieved. In its report, the commission defined sustainable development as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs"[1]. Early in the twentieth century Nicholas Georgescu-Roegen developed a model of global energy usage based on simple thermodynamic principles[2]. (figure 4.1)

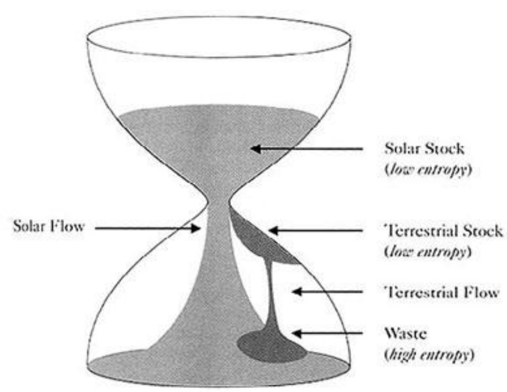

Figure 4.1: Georgescu-Roegen model[3]

All terrestrial energy sources, whether harvested biomass or fossil fuels, are inefficient at storage of raw solar energy. Both fossil fuels and renewable biomass fuels are formed from once living systems. Most terrestrial energy stores are in the form of fossil fuels which replenish at a negligible rate and therefore are not useful as a long term fuel source. Another downside to the combustion of fossil fuels is the release of carbon once sequestered deep underground. Unlike fossil fuel use, fuel from renewable biomass derives its chemical energy from the sun making it sustainable. Additionally, using renewable biomass has zero net effect on atmospheric carbon. For this reason fossil fuel alternatives such as biodiesel are particularly attractive for sustainability and preservation of the environment. While renewable fuel sources represent a major step forward in sustainability, the issues are not as clear cut as might be initially assumed. There are many factors that affect the impact that a particular technology has on the environment. These factors can confound and confuse attempts to discern the best course of action, but a clearer understanding of the relevant issues can help individuals to make better decisions on a local, national, and international level.

5. Historical Background:

Rudolf Diesel was born March 18, 1858 in Paris France, and his namesake invention was first tested over 35 years later. The first fuel to be used by Diesel was kerosene, and later petroleum, but his intention was to create an engine that could run on almost anything, including solid, liquid and gaseous fuels. He strove for this wide range of inputs because he sought for his engine to be as versatile as possible. Early diesel engines could handle a wide variety of fuels.[4] However, due to highly precise electronic injection systems designed to improve performance and efficiency modern diesel engines now have much more specific fuel requirements.

Diesel's original design was much different from the diesel engines of today that have been highly specialized for the use of petroleum based diesel fuel. This is the reason why someone today cannot run a modern diesel engine on vegetable oils; the method in which Diesel moved the technology of his engine forward was by giving the plans to inventors in return information on development. This, however, did not give Diesel the power to control the way the engine grew, leading development to drive towards petroleum because it not need to be preheated to such an extent.

In 1893 Rudolf Diesel ran the first experimental trial of a prototype power source.[4] His invention is now referred to as the diesel engine. In 1894, he filed for a patent for his invention. The first working prototype was constructed in 1897. In the 1940s, Colgate received a United States Patent for Biolipid Transesterfication. This process enabled more rapid production of glycerin and transesterified vegetable oil (biodiesel), which experienced increased demand in World War II.

The glycerin produced via this process was used to manufacture explosives and the biodiesel was used to power heavy-duty vehicles.

6. Conventional Transesterification Methods

The process of transesterification consists of exchanging the alcohol group of an ester compound with another alcohol. Biodiesel is formed by transesterification of vegetable oils or animal fats using a small aliphatic (see glossary) alcohols. Transesterfication may also be known as alcoholysis, or if methanol or ethanol is used, methanolysis or ethanolysis, respectively. The initial feedstock for biodiesel consists primarily of free fatty acids and of fatty acids bound to glycerol known as triglycerides. Waste vegetable oils and processed animal fats have a higher ratio of free fatty acids to triglycerides and must be processed differently then virgin vegetable oils in order to obtain a product of comparable quality.

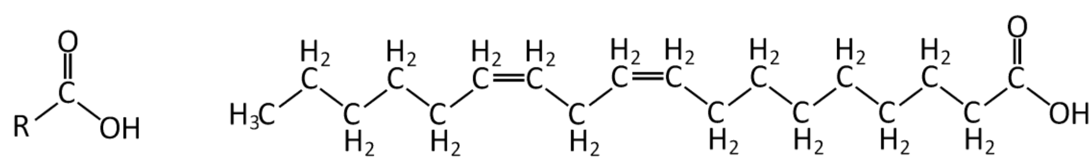

Figure 6.1: Molecular structure of fatty acid

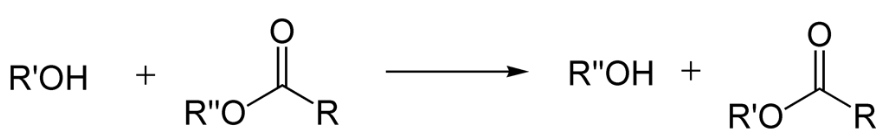

Figure 6.2 Transesterification.

When fatty acids react with a base they form soaps. This process is referred to as saponification. This occurs if any excess water is present during the transesterification process. This reaction consumes the base that is necessary to catalyze the transesterification process. In addition to consuming catalyst, the competing saponification reaction makes the separation of glycerol and biodiesel more difficult as soap functions as an emulsifier (see glossary).

Alcohols are molecules of the form R-OH. Typically small molecular weight alcohols such as methanol, ethanol, 1-propanol, and 1-butanol are used in biodiesel production. Methanol is the most commonly used alcohol in biodiesel production. However methanol production requires the use of methane from natural gases and is not sustainable. Ethanol is easily derived from plant sugars. The use of ethanol complicates the process as it tends to form emulsions and water-ethanol azeotropes making separation and recovery of ethanol more difficult.

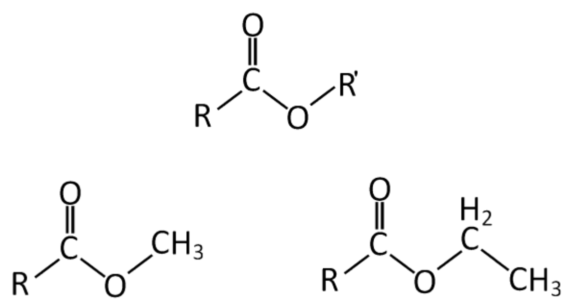

Figure 6.3 Molecular structure of Biodiesel - Top: general form, left: general methanol ester, right: general ethanol ester.

While diesel engines can run on biodiesel without modifications, doing so results in an approximate 5% power loss. This is because combustion is an oxidation reaction, and biodiesel is already partly oxidized.

Homogenous catalyst can be used to produce biodiesel. However the final product must be separated from the catalyst in a manner such that catalyst loss, biodiesel loss, and energy usage are minimized. Typical homogenous catalyst systems include base catalyzed, acid catalyzed, and two-step acid/base catalyzed. Acid catalyzed processes generally take the longest to complete and base catalyzed processes take less time to complete but unlike acid catalyzed systems these must contend with a competing saponification reaction. Generally base catalyzed systems are best used when free fatty acid content is low and are therefore suitable for production of biodiesel from virgin oil. When free fatty acid content is high a two-step acid/base catalyzed process is preferred. This minimizes soap production while maximizing biodiesel production. The first step consists of an acid catalyzed esterification, while the second step consists of a base catalyzed transesterification.

Base catalyzed systems can use any of the following bases: sodium hydroxide, potassium hydroxide, sodium methoxide, and potassium methoxide. In equimolar amounts potassium methoxide and sodium methoxide result in higher yields. Due to the competing saponification reaction process kinetics for base catalyzed systems are significantly more complex, resulting in the need for more complex models in order to produce an efficient process for manufacture.

7. Novel Transesterification Methods

Lipases are water soluble enzymes that catalyze the breaking of ester bonds in lipids. Using lipases rather than traditional chemical catalysts for biodiesel production is advantageous because much less catalyst is required. While the use of lipases for biodiesel production has been proven successful experimentally, it has not yet been implemented commercially. Due to the relatively high cost of lipase catalysts compared to traditional chemical catalysts, the use of lipases is economically unattractive. This can be solved by using enzyme immobilization techniques. These techniques can be applied to create a solid heterogeneous catalyst by binding the lipases to a solid substrate. Creating such a catalyst eliminates the need for catalyst purification and separation after the transesterification reaction is complete. One method of lipase immobilization is the creation of a sol-gel matrix. The creation of a sol-gel matrix impregnated with *Pseudornonas cepacia* (bacterium) derived lipase was shown to improve catalyst stability and functionally. In fact only 3mg of lipase was required for each gram of oil (0.3% catalyst by weight) and the reaction completed within 30 minutes. This compares to acid catalyzed systems which may require 5% weight catalyst and 4 hours to react until completion. [5]

While clearly advantageous compared to traditional biodiesel catalysts, there are several disadvantages to lipase catalyzed systems. Since lipases are proteins, and thus sensitive to chemicals and heat, one must ensure that the process used to bind the catalyst to the solid substrate does not significantly affect functionality. For the same reason, lipases must also be used at the proper pH, salinity, and temperature to function properly. Additionally, these binding processes are often complex and protein-specific, and therefore require extensive research and development to optimize. While some lipase-catalyzed systems perform well using water-miscible alcohols such as methanol and ethanol, this is not necessarily true for all lipase catalysts. Lipase catalyzed reactions that use homogenous catalysts, including the frequently studied C*andida antarctica* (yeast) lipase system, do not tend to work well with simple water-miscible alcohols. To make the process economically viable, alcohols such as 1-butanol and 1-pentanol must be used. These alcohols are typically derived from fossil fuels. In order to make these processes sustainable these alcohols must also be produced biologically. Research into fermentation-based production methods of such alcohols is currently ongoing.

Supercritical methanol methods are notable as they proceed to completion in minutes rather than hours or days and are physically catalyzed rather than chemically catalyzed. This process is very robust and can tolerate water in the feedstock and will convert free fatty acids to esters rather than soap. It does however require temperatures of 350°C and pressures of 45-65 MPa for up to four minutes (for reference atmospheric pressure is approximately 101KPa). While obtaining such pressures and temperatures requires a relatively large amount of energy, there are no energy costs associated with catalyst removal.

8. Corn:

The use of corn for biodiesel has been considered for many years, the concept of a renewable domestic source of oil is an especially enticing one. There are many possible benefits to doing so, including reducing reliance on foreign countries for fuel and decreasing our carbon footprint. An alternative to fossil fuels is becoming more essential as supplies are exhausted. If a long term substitute for these limited resources is not found, the increasing demand and the diminishing supply will eventually cause significant problems. While corn derived biodiesel can provide such a substitute there are many negative effects to its production, some of which are not immediately apparent. While biodiesel production from corn has been proven technically feasible there are many socioeconomic and environmental ramifications of its implementation. These problems limit the use of corn as a biodiesel feedstock.

The first major issue with corn-derived biodiesel is limited crop productivity. Corn is one of the least efficient sources of oil, yielding approximately 172 L per hectare compared to 446 L per hectare from soy and 5,950 L per hectare from palm.[6] When corn is diverted from food sources to gasoline production it has the secondary effect of creating a lower supply of corn in the food market. This inevitably causes a jump in price that adversely effects consumers around the world. Corn-derived food ingredients are common and include dextrose, high- fructose corn syrup, modified food starch, hydrolyzed vegetable protein, and xanthan gum; many products contain one or more of these ingredients. Additionally most meats, eggs and milk are also dependent on corn as it is a primary component of many animal feeds. Fuel diverted from food crops increases the basic cost of food which has the greatest effect on the poorest sectors of the world’s populations. This subsidization through diversion of food crops is passed on to the wealthier segments of society thus financing them in the creation of more capital at the expense of lower income segments of society. While total food consumption does not differ much between income levels, total fuel consumption increases markedly as income increases. This means that use of corn for biodiesel diverts wealth away from those with less wealth to begin with. This is made worse by tax dollars in the form of subsidies used to fund corn production.

The second major problem with corn based biodiesel is that whether or not it is as carbon neutral is far more dubious than other crops. In particular, what sets corn apart is the intensive use of nitrogen fertilizers. Nitrogen fertilizers have many environmental drawbacks. Most nitrogen fertilizers are derived from ammonia or dry ammonia products such as ammonium nitrate and urea. Ammonia is often synthesized using the Haber-Bosch process. The process is especially important because one third of the world food production is reliant on the ammonia produced through this method.[7] One of the drawbacks associated with nitrogen produced this way is that it requires large amounts of natural gas and is energy intensive. Natural gas represents up to 90% of the cost of the fertilizer production.[8] This makes the act of growing corn less carbon neutral and detracts from its attractiveness as potential feedstock for biodiesel. In addition to the initial costs of fertilizer one must also consider the financial and energy costs associated with transportation

One of the ethical issues in biodiesel production is the diversion of food crops to the production of fuel. In addition to the problems associated with food costs in the United States, the diversion of food to fuel causes problems in the world's poorest countries. Countries such as Mexico have been particularly hard hit when corn crops traditionally used for food have been converted to fuel sources. The price of basic food staples including corn and corn tortillas dramatically increased causing uproar in Mexico. This has primarily occurred through over-speculation by the controlling corporations in Mexico. The influx of cheap corn from the United States lowered the price of Mexican corn so that it could compete. The lower price allowed for it to be sold as a viable ethanol feedstock.[9] For low income individuals and families, an increase in food prices reduces their ability to purchase food, possibly making it impossible to afford enough for basic nutritional needs. In fact the situation has raised enough concern that Jean Ziegler, the UN Special Rapporteur on the right to food, called for a five year delay on biodiesel production.[10] Mr. Ziegler went so far as to say "It is a crime against humanity to convert agricultural productive soil into soil which produces food stuff that will be burned for fuel."[10] This type of issue also raises questions about the net effect of any given action. Economic instability and conditions of poverty can breed unfavorable social and political climates that can create unforeseen secondary and tertiary effects. The most prominent example being who would have expected the center stage the Middle East would be taking in world politics when oil was discovered there a little over a hundred years ago. One of the benefits of biodiesel is that it can be home grown and reduces the need for foreign fuel sources. This eliminates the inherent instability of purchasing energy from foreign countries. In addition if the economic system of a country relies on the starving of another country the system is also inherently unstable. Mexico is a great example with the passing of the “Food comes first” law, which limited exports of corn to counteract the rising costs associated with ethanol production[11]. In addition, history has shown that systems of energy procurement that involve procuring energy resources at the expense of the local populations inevitably lead to problems down the road. This particular issue is of considerable importance due to the close proximity of Mexico to the United States as well as their shared border and the already prominent immigration issue. The sustainability of US energy reserves relies not just on the current ability to produce fuel stores, but also on the long term feasibility and internalization of the industry and biomass producing capabilities within US borders.

In addition to the ethics pertaining to the diversion of food, the excess nitrogen from fertilizers used to grow feedstock poses significant environmental considerations. Excess nitrogen runoff from the agricultural processes ends up back in the environment and spreads far out and away from the fields it was originally used on. This transfer of nitrogen is represented by the nitrogen cycle (figure 8.1). Atmospheric nitrous oxide is a very powerful green house gas; each molecule of nitrous oxide is thirty times more potent than each molecule of carbon dioxide (CO_2).[12] In addition the runoff from nitrogenous wastes increases the rate of eutrophication (see glossary) in local bodies of water. Industries such as fishing and ocean aquaculture can be adversely affected by tidal blooms (see glossary). A common example of this is red tide which can be exacerbated by excess nitrogen runoff and buildup in marine ecosystems.

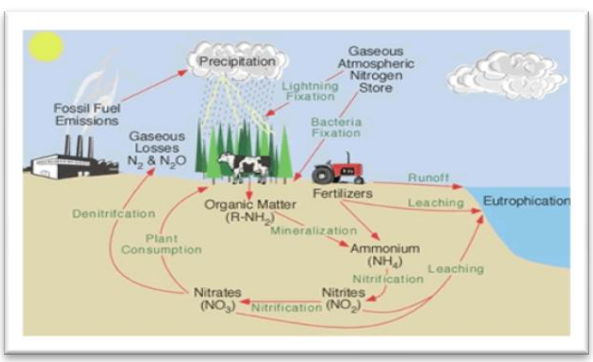

Figure 8.1: The Nitrogen Cycle [2]

One of the more substantial drawbacks to the use of corn as an input to biofuels in the United States is that most of the corn is grown in the center of the country. A majority of corn is grown in Iowa, Illinois, Nebraska, Indiana and Minnesota [13](figure 8.2), while these states only account for 9.631% of the total US population[14] . Currently all of the bioethanol production facilities are located near where a majority is grown. By extension it can be foreseen that biodiesel production facilities would be placed in a similar fashion. This by no means is meant to imply that biodiesel production facilities powered by corn should be located elsewhere, but a distribution of facilities similar to the distribution of BioFuel consumption would be ideal, for it would be minimizing the overall transportation cost to the end user.

Figure 8.2 Locations of BioEthanol Refineries in the US [15]

Corn's greatest strength, at least for now, is that it is very abundant and well established in the agriculture sector. In terms of an input, it is known almost exactly how corn can be produced, allowing biodiesel facilities to scale to that known input amount, minimizing excess or shortages in feedstock. While the centralized system of biodiesel facilities would not serve the nation as a whole because of the limitations on transporting the end product, this system would very much benefit the region where it would be located as bioethanol is today. The Midwest's location in the US in respect to coast line gives it a disadvantage in access to imported oil, much like the inverse of the situation stated previously regarding the transportation of corn-made biodiesel from the Midwest to the rest of the country. Corn then, as in input for biodiesel, would not be too unreasonable for the regions in which corn is grown.

Many waste products may be reclaimed from processed corn. The leaves, stalks, and cobs are known as "stover". It is common practice to leave the stover behind to decompose in the harvested fields, replenishing soil content and preventing erosion. There are certainly alternative uses, though one must pit those against the cost of infertile fields and possible soil erosion.

The individual stalks and leaves may be spun into strong twine, as the material contains large amounts of long fibers. This creates a valuable product, and in turn is a viable practice with which to bolster developing economies. The twine is ideal for use in paper products, clothing, and fashion (e.g. baskets, bags). Starch may be extracted from the stover as well, though most would be obtained through the cob. Starch is a valuable commodity, as it may be used as a cooking staple or even processed into biodegradable plastics. One such popular use is packing peanuts, as the starch-based foam provides excellent cushioning at a low, eco-friendly cost. Corn silk is a commodity product which may be harvested from the actual flower of the plant. Although this task requires special harvesting, it utilizes a product which would otherwise go to waste, and fetches a higher return as a nutritional supplement.

One use which has gained widespread notoriety is the use of both corn stock and waste in biodiesel/ethanol production. For reasons explained elsewhere, this particular use of corn stock is highly undesirable. However, it is possible to extract enough desirable material out of the stover to produce some quantity of fuel, though the stover possesses a higher rate of return when used otherwise.

While corn may return many valuable commodity products, they must still be weighed against the questionable use as a fuel. Though it certainly is possible to extract fuels from just the stover, it is unjustifiable. The cost would be too great for the minimal return, even factoring in the further use of the waste products.

9. Algae:

The term "algae" generally refers to a large and diverse group of simple photosynthetic organisms from the pylum *Chlorophyta*. Macro-algae are multicellular organisms colloquially known as "seaweed'' while micro-algae are unicellular organisms. The three most abundant types of micro-algae are the diatoms (*Bacillariophyceae*), the green algae (*Chlorophyceae*), and the golden algae (*Chrysophyceae*). "Algae" can also refer to members of the phylum *Cyanophyceae,* also known as cyanobacteria or blue-green algae.[16]

All types of algae lack the complex structures that are present in land plants such as roots, leaves and flowers. Algae however, do posses the same photosynthetic mechanisms that all other plants do. Given the relative simplicity of alga, algae with sufficient access to water, CO_2, and nutrients are generally more efficient at converting solar energy into biomass then any other flora. Micro-algae can be grown and harvested for bioenergy generation including production of biodiesel, biomethane and biohydrogen. Microalgae can also be used to captured and sequester CO_2.

It is possible to design an algal farm which when continuously provided with the proper feedstock is fully contained and electrically self-sufficient. An algal farm would require a number of integrated components as part of a larger plant design. The digester would convert animal wastes to methane rich, carbon dioxide rich gas. This gas production is sufficient to power a diesel engine AC generator pair which will be used to provide energy for the entire plant.[17] When methane (CH_4) of the generator exist gas is used it still contains a large amount of heat energy and CO_2. The heat can be used for drum dryer; the remaining CO_2 can be fed into growth ponds. Given the proper design, especially fluid flow, up to 90% of the CO_2 can be absorbed and in turn used by the algae. The filtered solid and liquids in the digester can be directly pumped into the growth ponds, in order to recover nitrogen, phosphorous, and trace minerals.

By matching growth rates and harvesting rates, growth ponds can be designed to operate in continuous steady state, where the harvesting steam uses agglomeration and settling to remove algae. The use of microalgae is beneficial in high growth rate ponds as it is easy to keep in suspension and requires little mixing energy. At algae to water weight ratio of approximately 1 in 5000, filtering the algae remains impractical as the algae will quickly clog the filter.[18] Both centrifuges and settling ponds are practical methods for separating and harvesting of the algae.[19]

Algal cultures are typically extremely productive and tend to accumulate biomass quickly when provided with sufficient nutrients. Given unlimited nutrients and space, growth would tend toward an exponential curve. This however rarely occurs in practice beyond a relatively short initial growth phase. The nutrient input is typically the limiting factor in algal growth. Classically, there are two main laws involved; Liebig's Law of the Minimum and the Blackman Limitation. The Liebig limitation states that growth is limited by the limiting nutrient. Therefore if all nutrients are supplied in continuous levels sufficient for growth at a specific level, then the reduction of a single limiting nutrient will proportionally affect quantity of biomass in the system after the steady state is reached. Note that according Liebig's limitation, nutrient restriction of this nature will not have any significant effect on the initial exponential growth rate before equilibrium is reached. The Liebig limitation can be observed in systems involving nutrient limitations of B12, phosphorous, nitrogen, and carbon, with various ratios being empirically established for various algal species. In contrast the Blackman limitation provides a description of the rate of biomass accumulation rather than how the process behaves in steady state. It states that if a system contains a fixed amount of nutrient the growth rate will be limited by that initial amount. The Blackman limitation is of little concern for macronutrients common to all algal species. However this limitation becomes significant if there is a nutrient that is not being continuously supplemented or accidently removed from the system.[17] This can occur in several ways such as supplying an incorrectly prepared growth culture deficient in a specific nutrient or nutrients. This can also occur when substituting a natural growth medium with an inadequate artificial one. In both cases the algal biomass will incorporate the limiting nutrient and remove it from the system.

Micronutrients are of particular importance when considering closed algal bioreactors and to some lesser degree also open systems (not of less importance but nature is not present to provide as it would be in a lake) In the following section some of the more important micronutrients will be overviewed as well as the particular processes they are involved in. Vitamin B-12 is a micronutrient that is mainly used in the production of DNA and fatty acid but is not easily synthesized so its cost to produce must be considered in a bioreactor or algal fuel plan. Individual algal use of vitamin B-12 is high but the potential for partial recovery of some of the vitamin after fatty acid removal. In addition B-12 can be made by bacteria in commercial processes, greatly reducing its chemical/carbon footprint(*Pseudomonas denitrificans* and *Propionibacterium shermanii*) Calcium is also used in the structural components of cell walls and cell membranes. Iron is another common micronutrient that is used in redox reactions as well as in DNA processes and sugar production

Macronutrients as the name implies are not necessarily qualitatively different but only differ in the amount that an organism needs them. A micronutrient or a macronutrient could easily be switched for two different organisms

Nitrogen in organic aqueous systems is present in many different chemical compounds. One factor affecting water pH is the ammonia/ammonium equilibrium. In this system ammonium is the conjugate base and ammonia is the conjugate acid. By nitrification, an alga converts both ammonia and ammonium to nitrates and nitrites and thus removes them from this equilibrium process. If an imbalance in the ratio of these two species results, Le Chatelier's principle (glossery), will drive the ratio back toward the initial equilibrium. When nitrogen is converted to biomass it is removed from the cycle.

The main source of phosphorus is through mining raw calcium phosphate ore and purifying it through industrial processes; therefore said processes must be evaluated for their carbon/chemical footprint. Drawbacks such as these should encourage scientists to open up new lines of investigation for more sustainable methods of producing raw materials such as using microbial bioprocesses for purification. Salt can be of particular importance in high salinity algae to help maintain homeostasis.

Atmospheric CO_2 (350 ppm) is not optimal for algal growth so its introduction and the cost of its purification and separation need to be considered for optimal growth of individual species. In addition the power costs of introducing the carbon dioxide must be evaluated.

The modification of light and dark cycles for algae can be a useful tool in algae production. The application of red light at certain key times during the algae’s light/dark cycle can modify its growth patterns and even its expression of its mating capabilities. This type of strategy can be useful if a single strain of algae is to be used and its growth in the system is more important that its reproduction or vice versa at any given time. For example while the population total is low, light/dark cycles can be manipulated to produce optimal reproduction. When the desired population is met, conditions can be modified once again to promote optimal individual growth.

In addition to algae’s incredible lipid production, they also have a great advantage over other inputs to biodiesel in that they are grown in a liquid environment, therefore requiring no arable land area for growth. This fact alone makes algae very promising considering the amount of food that is being diverted for biofuels to offset the requirement for the importation of petroleum. About 25% of the corn grown in all the US [20], that is drastically increasing the prices of those crops. This means that algae can be produced over land that is unusable for crop production, or land that has been depleted and is no longer suitable for production, or even in the middle of a city, leaving the arable land to be used for growing food.

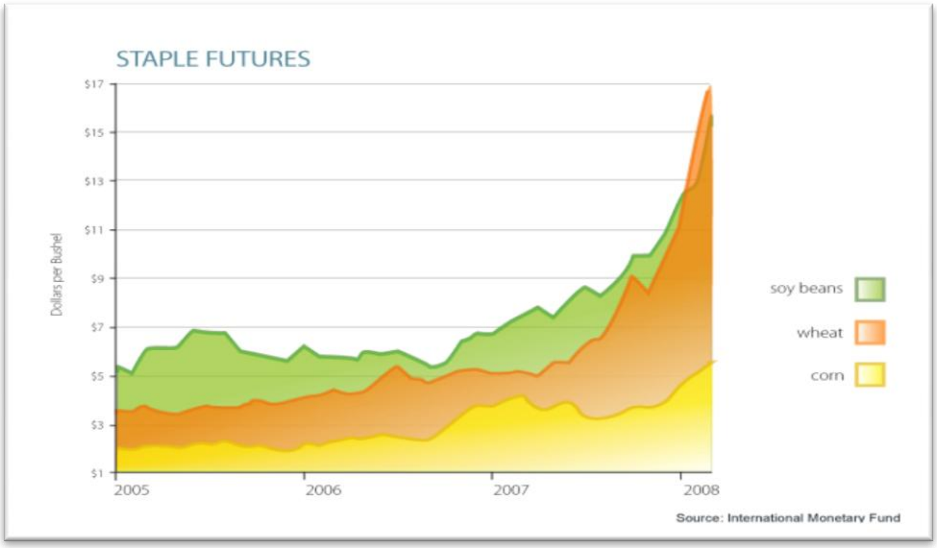

Figure 9.1: Futures of Biofuel related crops

The lack of land requirement and aqueous suspended growth environment gives algae the ability to be grown in a much larger spectrum of regions than corn, or any other crop-based biodiesel. This spectrum could include arid deserts, high elevations, urban areas and even on a facility in the open ocean. Although algae can grow almost anywhere, the high levels of sunlight that warm desert regions offer is ideal because of the sunlight's use in photosynthesis. Highly industrialized areas are another location where the production of algae would be not only effective, but would be synergetic with the industries that exist in the area already. This synergy would come from algae's ability to not only remove the carbon dioxide and nitrous oxide that is an output of many factories, but use it for its own growth when placed directly on the factories output. The minimal amount of space required to grow algae gives it the ability to be produced on the small business scale, a liberty not given by many other inputs from seed (or spore) to cylinders.

Algae's ability to be grown in a non-centralized fashion not only gives it an advantage in terms of maximum output capacity, but also an advantage in terms of national security of the energy sector. From malicious human actions to drought, the compartmentalized production of algae around the country would minimize stoppage of input to biodiesel production that is a caused by situations that are out of the hands of the producer. This separation of production would also have the benefit of lessening transportation costs of the final product to the end user, reducing the overall cost of the product.

10. Green Crude:

One incredibly promising step in alternative fuels is the production of what is known only as “Green Crude”. It should immediately be noted that Green Crude is not a biodiesel or ethanol fuel, but a chemical equivalent to the light, sweet crude that is sent to distilleries. [21] While the formula is currently protected under trade secret, Sapphire Energy has already used their formula to power an airplane in a cross-Atlantic flight. The other two competitors in the Green Crude market are Solazyme and Aquaflow. Though initial speculation cast a shadow on the future of this product, steady investment gives much hope for successful development and commercialization.

Green Crude stands to be the biofuel of the future for a few key reasons. The first is again the fact that Green Crude is neither biodiesel nor ethanol fuel. Therefore, no existing petroleum infrastructure (from cars to petrofuel refineries) would require modification in any way. Reduced emissions are also an incentive, as the carbon exchange from growing to combusting is neutral. In other words, the Green Crude releases the same CO_2 that the algae capture~~s~~ during photosynthesis. This would at least halt further CO_2 production from petroleum-related energy use. Green Crude is produced by brewing material such as discarded plant matter and sewage into an algae bloom. From here, the brew undergoes certain processes which result in Green Crude and clean water. Therefore, the production of Green Crude also produces potable water and has the potential to clean up existing water pollution.

Though ultimately it is desirable to develop non-combustion based fuel sources, Green Crude appears to be an intermediate step. Though it would take time, Green Crude has the *potential* to displace all petroleum-based fuel use. The use of Green Crude would halt further atmospheric CO_2 production from the combustion of petroleum fuel, and can be used to treat water pollution and produce clean water. Lastly, algae-based fuels do not displace any land acreage dedicated to food crop production. Therefore, socioeconomic impact is limited. All of these reasons show Green Crude to be just as viable as valuable in the search for sustainable alternative fuel.

11. Recycled Product:

Like algae, the use of recycled goods would not require any land to grow, aside from that required by new facilities designed for the production of biodiesel. The recycled good in focus, used coffee grounds, has some advantages over other recycled inputs. Compared to other inputs, namely used frying oils, coffee grinds are largely an untapped resource, therefore giving it much potential in terms of increase of overall biodiesel production with the insertion of coffee grinds as a supplemental input. In 2000 it was reported that Americans drank an average of 4.07 Kg worth of coffee, compared to the EU average of 5.27 Kg, 6.74 Kg in Germany, and 9.15 Kg in Scandinavia[22], so this input should also be considered on an international level.

Another of the benefits to coffee grinds is that along with being produced by businesses, they are produced in most households, offering an opportunity for most Americans to directly take part in the savings that would undoubtedly be returned to them with the recycling of their coffee grinds. This, in turn, would vastly benefit and ease the collection of used coffee grinds on the local level, as well as expedite the process of making people aware of coffee grinds as an input by way of economic incentive.

Within the past few years, researchers have developed a method of extracting oil from spent coffee grounds. Quantitative testing has revealed that oil can be extracted from spent coffee grounds at rates between 10-15%. [23] There are many benefits to using spent coffee grounds as a feedstock for biodiesel, resulting in a potential of 208-million gallons of additional fuel per year (based on global coffee consumption)[24]. One interesting benefit is the stability of oil derived from coffee due to the higher anti-oxidant levels present in the material. The resulting increase in shelf-life makes coffee-based biodiesel suitable for industrial operations (defined as stable for at least one month). Once the oil has been extracted and converted, the now twice-processed feedstock may be further utilized as normal. This includes pressing into fuel pellets, ethanol feedstock, or using as compost/fertilizer. Though Starbucks is known to give away spent coffee grounds to their customers for use as fertilizer, it is determined that they could instead make as much as eight-million dollars per year by processing the grounds according to the methods above (converting into oil and selling both biodiesel and spent grounds as commodities).[26]

Researchers are also looking at citrus peels as a source of ethanol fuel. Although it is now known that corn-ethanol requires more energy to produce than it releases, scientists hope that this is not the case with citrus-based ethanol. This could be valuable in localized areas such as Florida (which is known for its vast orange groves). [25] Also of interest is the Coskata process, which operates on the principle of gasification. Waste organic material is processed into a uniform blend which is then converted into a gas. This gas is converted into ethanol, which is then separated and removed. [26] This process is potentially valuable as any organic waste may be processed into ethanol in an efficient manner.

One of the obvious and major benefits to using recycled materials and trash to produce biofuels is that they do not require agricultural inputs and because they are a readily available and a renewable resource. However, the use of recycled materials does have its drawbacks. For example unless the material is pre-separated, extracting the usable materials from common debris can be an energy-intensive process. In addition to the normal considerations for biofuels, the use of recyclable materials has the added benefit of freeing up land area from dumps and landfills, which prevents methane off-gassing. In addition it can limit environmentally unfriendly practices such as offshore dumping. The use of waste products also minimizes costs surrounding the initial input to grow biomass. Moreover, if cellulosic breakdown and traditional fermentation processes were used on plant debris, left overs, spoiled food, and the byproducts of cooking as well as other organic materials, the world as a whole would be able to make major steps not only to energy sustainability but also to overall sustainability.

The diversion of waste from landfills helps to minimize green house gas emissions from facilities that off gas methane (CH_4), which contributes thirty times more green house gases (GHGs) effect to the atmosphere than CO_2.[11] In addition, preexisting facilities can be converted to capture and store methane for use in biofuels. Such adaptations can help to reach a more integrated national fuel supply. In addition to its capture at current facilities the production of methane can be easily done through the use of fermentors, which allow for biodegradable material to decompose often by providing a hot place to catalyze the process. This particular type of modification is also particularly worthwhile because the gas coming out of landfills is often just burned off, leading to increased GHGs. Recycled materials can also be used in other stages of the biofuel processes to keep them from entering landfills. For example composted waste can be used as a nutrient source for traditional biodiesel crops in the form of fertilizer. Fertilizers made from recycled materials would represent a major advancement over the traditional use synthetically manufactured substitutes.

12. Conclusion:

Our findings show that the future of biodiesel clearly lies in the investment of an algae based infrastructure. This is apparent not only from the efficiency of algal biomass systems, but also that algae can be grown very densely and in inhospitable environments unsuitable for food production. This factor is of particular importance because it bypasses many of the socioeconomic and ethical issues associated with using food crops and large amount of land area for fuel. Implementation of an algae industry concentrated on biodiesel production on a large scale has not yet been established so its technical feasibility has not yet been practically determined. As additional investments and innovations occur and the price of conventional fuel products increases the viability of large scale long term algal biofuels production will increase. New technologies may completely change the face of energy production, and petroleum-based fuels may be rendered obsolete in the foreseeable future.

13. Glossary

Aliphatic: An organic (carbon-containing) compound that does not contain a benzene ring.

Azeotrope: A mixture of liquids with identical vapor and liquid mixture compositions, resulting in a boiling point distinct that of any constituent liquid. These cannot be separated by simple distillation. In this report, “azeotrope” is specifically used to describe the mixture of 95.6% ethanol (boiling point=78.4°C) and 4.4% water (boiling point=100°C) by weight which boils at 78.1°C.

Catalyst: A chemical that modifies the rate of a chemical reaction without being consumed by the reaction. All catalysts referred to in this report speed up the chemical reaction. Catalysts may be homogeneous or heterogeneous. Homogenous catalysts are the same phase as the reactants, while heterogeneous catalysts are different phases then the reactants. In transesterification homogenous catalysts are liquid or aqueous while heterogeneous catalysts are solid or sol-gel matrixes.

Emulsion: A mixture of two or more normally immiscible (unmixable) liquids. *Emulsifiers* such as soaps promote the formation of emulsions.

Enzyme: A biologically derived protein catalyst.

Esterification: The chemical reaction which forms esters. In this text, "esterification" will often be used to describe a Fischer esterification which is characterized by the combining of an alcohol and an acid catalysis to yield an ester plus water.

Eutrophication: An increase in chemical nutrients, specifically nitrogen or phosphorus containing compounds. Because these compounds usually limit plant growth an increase will often result in excessive plant growth and decay. This increase in an ecosystem's primary productivity results in depletion of oxygen and a severe reduction in water quality in aquatic ecosystems.

Feedstock: The raw materials required for a chemical process.

Haber-Bosch Process: The production of ammonia via the nitrogen fixation reaction of nitrogen gas and hydrogen gas requiring enriched iron catalyst.

Le Chatelier's principle: A Chemical principal which states that when a chemical system at equilibrium experiences a change in concentration, temperature, volume, or total pressure, then the equilibrium shifts to counter-act the imposed change.

Tidal Blooms: A rapid increase in the algae population of a body of water. A tidal bloom is usually identified by a change in water coloration from the extremely large amount of algae present in the water.

Sol-Gel Matrix: A matrix that changes from a colloidal suspension to a polymer matrix with decreasing hydration levels.

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