Zero Waste Biodiesel: Using Glycerin And Biomass To Create Renewable Energy

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ABSTRACT

Biodiesel production creates glycerin as a byproduct. Although glycerin does have its commercial uses, even the current modest biodiesel production has outstripped US glycerin demand. We have combined this excess waste glycerin with waste biomass to produce combustible pellets as an alternative to coal for energy production. Our pellets produced an energy yield of ≈16 kJ/g, placing their energy content within the expected range for existing fuel pellet infrastructure. The pellets can be viably manufactured using simple manufacturing equipment, and can be combusted as fuel in existing fuel pellet and Coal burning facilities. This will greatly facilitate pellet production and adoption as an alternative fuel source in our increasingly resource-conscious world.

FACULTY MENTOR

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Sean Brady and recent graduates, Gregory Leung and Christopher Salam, are truly an inspiring team of committed, intelligent and professional individuals; it has been a pleasure being their faculty mentor. What started as an inspiration to fuel campus transportation vehicles with biodiesel manufactured from waste oil from food services, led the team to examine other waste streams that exist from the biodiesel process and other biomass waste materials available on campus. This waste stream analysis segued into a project that would investigate a potentially new fuel source of energy derived solely from waste materials. As the capstone senior design instructor and instructor in Green Engineering, I found this idea to be innovative because it featured the accounting of multiple waste streams in various life cycle analyses with a potentially beneficial result with immediate impact. As their faculty mentor, I provided guidance in their experimental design and framework of the project and mentorship as they developed proposals for student design competitions. The idea and work presented here earned recognition at the 2007 WERC environmental design competition with a U.S. Department of Agriculture award for innovative use of agricultural materials and a Phase I award at the 2007-2008 EPA P3 student design competition.

AUTHOR

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Sean Brady is a graduating senior in Environmental Engineering, with a focus on water conservation and resource management. His industry experience includes asphalt quality control, waste water plant operations, and perchlorate remediation. Although Zero Waste Biodiesel itself is more "material and energy management," it dovetails nicely with the central themes of smart, low-waste processes and the transformation of waste streams into useful products. Sean is currently pursuing his Professional Engineering License, and after graduation he will continue his engineering career in New Mexico, with his wife and two children.

(Special commendation goes to two recent graduates who were a part of Sean's research team. ***Christopher Salam,*** *'07, is currently a graduate student at the University of California, Davis, studying renewable energy sources.* ***Gregory K. Leung,*** *'07, is a practicing engineer.)*

ZERO WASTE BIODIESEL: USING GLYCERIN AND BIOMASS TO CREATE RENEWABLE ENERGY

Sean Brady

Introduction

Biodiesel is a popular alternative fuel. It is carbon neutral, has emissions equivalent to or below diesel, is biodegradable, non-toxic, and is significantly cheaper to manufacture than its petroleum equivalent. However there is one significant drawback: for every 10 gallons of biodiesel produced, roughly 1 gallon of glycerin is created as a byproduct.

Although glycerin does have its industrial uses, current biodiesel production has already exceeded market demand, leaving large amounts of practically worthless glycerin in the manufacturers' hands, leading to increased disposal costs. We show that by combining waste glycerin with waste biomass (corn husks, wheat chafe, etc.), we are able to produce pellets which can be easily and inexpensively manufactured, are suitable for existing combustion energy plants, and are a superior alternative to coal.

Glycerin Pellets

The idea of combining the waste glycerin from the biodiesel process with biomass is relatively new and no other projects using this idea have been published. The concept originated on a Biodiesel Internet forum where home brewers were brainstorming ways to utilize their excess glycerin. Many users discussed creating soap, lotions, and using the glycerin in food products, but many of these processes require purification, a chemically unstable process, and are inherently low-volume and low-demand. Other uses for glycerin include selling it to a company which refines glycerin for use in food or pharmaceuticals. While once profitable, the current abundance of glycerin is such that there is little money to be made, and often money to be paid, in having a company pick up your glycerin. However one user caught our attention with the words "glycerin logs," to be burned in traditional fireplaces. Although glycerin logs were ultimately unfeasible, it started us thinking about ways to create solid form, easily portable fuel sources for combustion energy. We ultimately found a way to absorb two waste streams, thereby enabling biodiesel production, by creating a product which could reduce the coal dependence in the world.

Figure 1. Sample pellets containing biomass (sawdust) and glycerin in a ratio of 1 to 1.3.

Biodiesel

Biodiesel has been well explored by industry and in academia for at least 30 years. As biodiesel is broadly-defined as any chemical that is a methyl ester, an acceptably vague definition because of the wide range of chemicals which can be combusted in a diesel engine. Due to this flexibility of definition and use, many different methods can be employed, even some that do not create waste glycerin. These processes, however, have their drawbacks.

These often do not create a significant quantity of byproduct, and are usually terribly energy intensive. Often times the thinning procedure also leads to a weaker or undesirably volatile fuel. The major methods for creating a less viscous fuel from vegetable oil are dilution, micro-emulsification, pyrolysis, and trans-esterification[1]. Pyrolysis is fairly energy intensive, and leads to a loss of feed. Dilution and micro-emulsification processes will lead to lower quality fuel, and have large initial material costs. Trans-esterification, or the thinning process that chemically lowers the viscosity of the mixture, sticks out as an economically reasonable process, especially if a market can be established for the post process glycerin. Lately, biologically-based reactions, such as lipase-catalyzed processes for creating biodiesel, have

Figure 2. Biodiesel glycerin mixture

also been explored.[2] A variety of research on the qualities of the feed stock on oils has been conducted.[3] Due to the drawbacks of these processes, it would be preferable to remain with traditional biodiesel production, and simply find an adequate use of the waste glycerin.

The biodiesel synthesis method that we used to great our biodiesel and waste glycerin is a trans-esterification process, which combines an alcohol as a thinning agent, and a strong hydroxide as a catalyst, with vegetable oil to create a viscous combustible liquid, shown in the top layer of Figure 2. The bottom layer is the waste glycerin which is our primary concern. Note that the 10:1 production ratio of biodiesel to glycerin is not accurately shown in the image.

Refuse Derived Fuels (Rdf)

The creation of waste pellets is already a significant industry in the developed world, converting waste from material and food industries to create compressed pellets suitable for combustion as an energy source. The manufacture of a pellet is easy to automate. In addition, the process often does not require heat input or a chemical change, and as such can be manufactured quickly. Many of these pellets are used in combustion plants, and therefore do not need extremely costly food-grade processing.

These manufactured pellets are called refuse derived fuels, or RDFs shown in Figure 3, and are primarily combusted within power plants for energy purposes. Considering the vast array of materials already being formed into RDF and the ever-increasing demands for energy, there is plenty of room in the market for an additional source.

Results

Project/Design Approach

Pellet formation is fairly straight forward. The raw materials (waste glycerin and waste biomass) are mixed by weight ratio and blended by hand in a large mixing bowl. Various ratios of glycerin(38.5g and 31.3g) to waste biomass(50g) were then mixed to produce a crude unfinished material. The pellet mixture (approximately 12g) is placed inside a rolled piece of newspaper wrapping, and the ends are folded down so that both ends of the cylinder are covered. No adhesive is used, and until the pellet is compressed this unit will remain prone to unwrapping. This

Literature Values: Fuel Source	Energy (kJ/g)
Coal [4]	15 – 27
Coke [5]	28 – 31
Dry Wood [6]	14.4 – 17.4
Gasoline (octane) [3]	47
Diesel [3, 7, 8]	44.8 – 47
Bio-Diesel [3, 4]	41.2
Natural Gas (CH_4)[3]	56
Ethanol [3]	29.7
H_2 [3]	142
Tires	28.5 – 35
Waste Plastic	29 – 40
Household Waste (RDF)	12 – 16
Household (RDF)	13 – 16
Demolition Waste (RDF)	14 – 15
Paper Sludge (RDF)	12.5 – 22
Waste Wood	15 – 17
Dried Sewage	16 – 17
Animal Waste	16 – 17
Commercial Waste	16 – 20
Industrial Waste	18 – 21

Theoretical Values: Fuel Source	Energy (kJ/g)
1:1.3 Biomass/glycerin (manure 60%, trimmings 35%, leafy material 5%) (theoretical)	11-24
1:1.3 Glycerin/Sawdust Pellet (theoretical)	16.94
1:1.6 Glycerin/Sawdust Pellet (theoretical)	17.1

Experimental Values: Fuel Source	Energy (kJ/g)
1:1.6 Glycerin/Sawdust Pellet (theoretical)	16.9

Table 1. *Energy Content of Fuels*

Figure 3. *A sample picture of a refuse derived fuel (RDF)*

Figure 4. *Presented are the components used to make the biomass glycerin waste pellets.*

raw pellet is transferred into the mold, a short length of PVC with one end sealed. The diameter of the PVC pipe is 12.5 mm, and its length is four inches. The mold helps the pellet retain its cylindrical shape while a short metal rod, slightly smaller than the PVC internal diameter, is inserted into the open end of the mold to compress the pellet. Pressure was applied by hand, approximately 250 psi for 15 seconds. This pressure not only reduced the pellet size, but also encouraged the glycerin to permeate the materials and form a single firm unit. It should be noted that this form of production is only used in initial laboratory experiments and actual commercial production will of course be large scale and automated. Figure 4 shows the components that were used in the bench scale process.

A key element of this project is energy estimation of solid matter via calorific testing. Without a laboratory-quality bomb calorimeter, this test was conducted by combusting the material in an aluminum 'boat,' floating in water, in a well-insulated container.[9] While conducting this process, it was found that additional oxygen was needed for sufficient combustion to occur. The reaction eventually consumes the solid matter, and the temperature change experienced in the water is recorded and placed into the specific heat equation to find the energy content for the mass of the pellet. After multiple runs of failed calorimeter results due to accidental combustion of the container, wetting of the mixture, and failure of the squib to ignite, a single somewhat accurate quantitative estimate of the energy content of the solid was obtained, and is included in Table 1. Additional tests were not possible due to limited resources, mainly having used all available oxygen and squibs. (Update: As of the time of publication, access to a functional lab calorimeter has been obtained, and ongoing research is underway. Initial results proved our efforts worthwhile, coming in at 15.4, 15.6, and 15.2 kJ/g and displaying a respectable error rate of only 10% for our ad-hoc apparatus. These results will be part of a larger report to be published at a later date.)

Error Analysis

In considering possible sources of error in this design, the only area of concern lies with our ad-hoc calorimeter and its ability to estimate energy content. If a proper calorimeter was available, the data, and our estimates derived thereof, would be much more reliable. Additional deviation would arise from variations inherent in the waste biomass, but given the medium (RDF pellets) the energy output is expected to vary slightly unit to unit. Additional testing to determine the exact variation to be expected will be performed once an adequate calorimeter is obtained.

Results

The energy values for glycerin waste pellets and competing energy sources are shown in Table 1, showing that theoretically and experimentally, the glycerin waste pellet is a very suitable source in replacing or supplementing low end coal and RDFs.

Discussion

Economical Impacts

The economic aspects of this project are perhaps the most readily understood and appreciated. The fact that biodiesel is less expensive to produce than petroleum-based diesel is a significant contributor to biodiesel emerging popularity. However, those costs do not include costs associated with storage or disposal of waste glycerin, a consideration which is going to demand significant attention as biodiesel production increases. Laboratory-based biodiesel production on a small scale can cost less than a $1 a gallon; however, in a large scale biodiesel plant, with associated licensing and fees, production can cost $1.13 - $2.60 depending on the quality of the materials used. With waste oil (used cooking oil) the cost is expected to not exceed $1.58.[10] As discussed, the solid fuel pellets created with the waste glycerin provides a market for the glycerin, and may even offset the cost of biodiesel production itself. Potential consumers include sealed combustion residential heating units and all current RDF pellet customers.

Economic concerns include both short and long term costs. The short term cost from transitioning from petroleum to biodiesel and glycerin-based electricity production may require a modest investment in capital and man-hours, however the long term benefits to a developing nation and global prosperity far outweigh the short term costs. Global agricultural and energy economies can prosper from the increased reliance of biodiesel and its glycerin waste. An increased demand in the raw products that are required for biodiesel production will positively affect existing industries. By utilizing glycerin in energy production, dependence on petroleum can be reduced, thus reducing greenhouse gases even more.

Social Impacts

The main goal of this project is to harness the discarded materials of a growing urban biodiesel industry. This will lead to an increase in bio-fuel desirability, and people will only stand to gain from a new, cheaper fuel that can be harnessed within the same infrastructure with which they are comfortable. This will help both developed and developing nations.

> In developing nations, where modern conveniences are not always accessible, many more unorthodox methods are already being used to obtain fuels.[11] Developing countries see bio-fuels as a means to stimulate rural development, create jobs, and avoid foreign exchange tariffs.[12]

In developed countries, which have significantly entrenched fossil fuel infrastructures, biodiesel has already been proven to be a significant success. In the United States, domestic production is over 30 million gallons a year.[13] This fuel has been proven to be very useful, since diesel consumption is greater than 60 billion gallons per year.[14]

Regardless of the market, biodiesel synthesis generates a glycerin waste product, of up to 20% of the feed.[15, 16] This waste product is becoming the primary, perhaps the only, major problem with biodiesel large-scale manufacturing. This begs the question, “What is being done with the glycerin waste product?” Fortunately glycerin is also biological and biodegradable, as often times the product is thrown out or composted. There are some uses for raw glycerin in industry; however there are many more uses of glycerin after a number of purification steps. Much of the one million gallons of waste glycerin produced each year is incorporated into functional products, such as soaps and cleaning products, but it is essential that these purifications be made. Without purification, biodiesel glycerin waste contains methanol as well as a significant amount of salt content that make it difficult to be placed into isolated glycerin reactions. The challenge is to keep purification costs low and the process sustainable while still being able to produce products that would be less expensive than the current methods of glycerin alteration.

Since both of our input streams are waste streams, waste glycerin and waste biomass materials (corn husks from the Midwest agriculture), the only costs applicable will be for transportation and storage of the material and product. This product has the potential to be an industry-wide coal substitute or another type of RDF, as it is already being used in Midwest power plants.[17] Burning our glycerin-cellulose product lasts three times longer than burning the same amount of regular fire wood.[2] All in all, our process proposes to absorb two waste streams into a marketable end product that reduces use of coal and leads to a environmentally friendly planet.

Environmental Impacts

Biodiesel has been shown equivalent to diesel not from a performance and efficiency standpoint, but has also been shown to cut overall emissions by 45% or more, and leading to significant decreases in all non-NOx gases.[18] Biodiesel is non-toxic, quickly biodegradable, and made from a carbon renewable source. A large number of epidemiological studies from different parts of the world on air pollution from gasoline have consistently identified an association between ambient levels of air pollution and various health outcomes, including mortality, exacerbation of asthma, chronic bronchitis, respiratory tract infections, ischemic heart disease, and stroke.[19, 20] Using this product would not only reduce the coal burned, but also lead to an increased use of biodiesel, thereby improving air quality and reducing the immediate health effects on the population.

> At present, the United States requires nearly 61 billion gallons of diesel fuel; if in the future biodiesel makes up 3% of the diesel fuel pool, over 1.8 billion pounds of glycerol will be produced as a byproduct which greatly exceeds the current demand of 0.49 billion pounds glycerol. [21]

We hope that our work with glycerin will lead to a significant rise in the use of biodiesel not only from the surrounding community but in a global sense. Since this project is structured around waste products, there is no ultimate sacrifice or risk that the society has to make concerning biodiesel adoption.

The biomass glycerin fuel pellets will burn cleaner than the coal currently used as fuel in many industries. Additionally, two pre-existing waste streams will be used to make the pellets, requiring no new raw materials. Also the energy required to make the fuel pellets will be substantially less than the energy required to produce coal. Most importantly, the fuel pellets will be a nearly carbon-neutral fuel, meaning that the carbon that is released into the atmosphere when burned is carbon which has already been in the environment. It would not be carbon released from fossil fuels, which is carbon that was no longer in the environmental carbon cycle, causing the harmful net gain of carbon dioxide which has been shown to be overall associated with global warming. [22]

Health, Safety, & Hazards Assessments

Biomass (sawdust, manure, grass clippings and corn husks.) is a very benign and chemically-inactive material. There are no hazards that are associated with it, aside from accidental ingestion and possible splinters during handling. Glycerin is also not a health concern. Although glycerin is a component in many products and pharmaceuticals, the glycerin which will be used in this process in not food grade. Therefore basic precautions regarding handling and storing glycerin should be followed to avoid unintentional consumption.

Pellet production is of little health concern, although glycerin-biomass pellet combustion may present a hazard. Glycerin combustion at low temperatures encouraged the formation of acrolein, a toxic gas. Acrolein (2-propenal) formation does not occur when under high temperature combustion (700°C) characteristic of a plant that burns biomass as a source of energy. Acrolein may be cause for concern when the biomass glycerin pellet is left to smolder or burn at low temperatures (280°C), as might be expected in an ornamental residential hearth.

Acrolein can be deadly in concentrations of 10 parts per million. The chemical is toxic if swallowed, inhaled, or absorbed through skin, and is a potential carcinogen. The vapors of this chemical can be irritating to the eye, nose, and throat, and contact to the skin or other body parts can cause burns.

For the residential market, the pellets would only be available to the high temperature, sealed, properly-ventilated furnaces available on the European market. In an industrial setting, secondary measures should also be in place such as a contained combustion chamber and post-process scrubbers and incinerators, which also mitigate environmental risks. Of course traditional emissions such as carbon dioxide, carbon monoxide, nitrogen dioxide, and similar combustion process emissions are also produced; however these are not immediately toxic and should be removed by the scrubbers as well.

Conclusion

In conclusion, this design project was pursued with the hopes of promoting biodiesel and sustainability. In order to create an effective energy source, this group has explored the combining of two waste streams, biomass and biodiesel waste glycerin, to form an energy source that is equivalent to refuse derived fuels (RDFs) in energy content. Additionally, this process will lessen the impact of refuse on landfills and reduce our dependence on fossil fuels. Our project has shown that the energy content of the bench scale test is similar with the theoretical energy content that was calculated. The verification of energy content shown in our bench scale process can easily be reproduced in an industrial scale, where a pellet making module can be attached to a biodiesel plant. The module has a payback period of 10 years where after 10 years a profit will be made. The fixed capital investment needed for this attachment facility is $4.85 million. This cost is relatively low, making this project a feasible idea that can be commercialized, easily. With further research and design, this concept for creating an effective source of energy from these waste streams can be applied and improved further to industry and eventually become a viable commercialized product

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Endnotes

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[9] The Bomb Calorimeter consisted of a 2'x1'x1.5' styrofoam ice chest filled with 200 mL of water. Weighed quantities of the glycerin/biomass mixture was floated in an aluminum foil boat, and the ice chest lid was placed on top and taped. The atmosphere was flushed and replaced entirely with pure oxygen, and then the pellets were ignited with a squib. The water temperature was measured prior to ignition, and after combustion. Many iterations were needed to come up with this one design that worked somewhat properly.

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