THE CHEMISTRY AND HISTORY OF BIODIESEL

Biofuels are in the news as an answer to reducing our dependence on foreign oil and petroleum based fuels. Biofuels are fuels that are derived from plant material such as soy oil or animal fats. The sources of these fuels are varied. They can come from plant oils derived from many different crops, and fats from slaughter houses and restaurant wastes.

Biofuels represent an ecologically friendly source of energy that is replaceable, unlike petroleum based fuels which are not. In many cases these fuels represent the saving of energy from waste material that would be thrown away and discarded onto a waste dump.

The use of renewable energy sources instead of fossil fuels is a new and exciting field of endeavor, or is it?

The fact is that the use of biofuels predate the use of petroleum based fuels for internal combustion engines. The diesel engine was designed to run on vegetable oil and the model A ford was designed to run on ethanol (alcohol).

At the time that the diesel and gasoline (internal combustion) engines were developed, the world was an agrarian society of small farmers. Both Rudolph Diesel and Henry Ford saw the economic benefit to the farmers and a good and plentiful source of fuel for their engines. (1)

HISTORY

• An engine converts heat energy into mechanical energy to do work.
• The gasoline internal combustion engine (Otto cycle) was invented in 1876. The original engine was very inefficient with less than 18% efficiency.
• During the 19th century, the steam engine (external heat source) was the predominant engine although it was a heavy resource consumer and very inefficient, only 12%. (1)
• Early in the century Nicolas Carnot described the ideal internal combustion engine. He stated that the term “perfectly efficient engine could not be applied to any heat engine.” (2)
THE CARNOT CYCLE

The Carnot Cycle represents the ideal heat engine (internal combustion). All gasses increase in temperature when compressed and cool when expanded. When no heat is exchanged it is called “Adiabatic”. When the temperature is kept constant it is “Isothermal”.

- Nicolas Carnot (1796-1832) believed that in an engine all heat could not be converted to mechanical work. Carnot believed that the efficiency of any heat engine depended on the difference between the highest and lowest temperature reached in one cycle. The difference being proportional to the efficiency of the engine. (2)
- This is the basis for computing the efficiency of each cycle for all heat engines. The larger the temperature difference, between the combustion temperature and the exhaust, the more efficient the engine.
- Rudolph Diesel, using the work of Carnot (the Carnot Cycle), developed an engine in 1892 that revolutionized the engines of the day. (1)
- In a gasoline engine a mixture of fuel and air are injected into the engine and compressed, after which the mixture is ignited with a spark which expands the gasses and drives the engine.
- In a diesel engine only air is compressed, to a much higher pressure than in a gasoline engine. When the air is so compressed it becomes hot enough that when fuel is injected at the high pressure it ignites spontaneously driving the engine. The original engine had an efficiency of 26% almost double that of the gasoline engine. Today they operate at a much higher efficiency. A gasoline engine compresses at a ratio of 8:1 to
12:1 while a diesel compresses 14:1 to 25:1 this leads to better efficiency. (3)

- Diesel demonstrated his engine at the Paris world Fair running on peanut oil. He and Ford thought that the utilization of biomass fuel was the real future of his engine. (1) Biomass is any biodegradable material derived from living things weather from plants or animals.
- Petroleum based fuels soon replaced the biomass fuels due to price, government intervention and availability.
- The business tactics and wealth of the petroleum companies influenced the development of the engines, and their construction was altered to accommodate the new cheaper fuel erasing the potential use of biomass based fuels.
- The early engines were very heavy and large and their usefulness was in shipping (eliminating coal) and submarines which the Germans were building in large numbers.
- Rudolph Diesel literally disappeared in 1913. There are questions about his death. He did not agree with the politics of Germany and the use of his engine in their Naval fleet. This would allow the German submarine fleet to be driven by his diesel engines. He was on his way to England to arrange for them to use his engines when he disappeared. There are many theories on how he died or was assassinated. (1).

PETROLEUM BASED FUELS
- Petroleum is a mixture of many different organic compounds called hydrocarbons, as they are composed of only carbon and hydrogen. As a result fuels based on it are themselves mixtures. In the refining process the petroleum is distilled. As the compounds with different carbon contents boil at different temperatures, they are separated by that means. The lightest compounds are all are gasses, methane (natural gas), with one carbon through butane with 4 carbons. C5 through 7 are solvents followed by Gasoline, Kerosene, and Jet fuel. C12 to C20 are fuel oil and diesel. Above that are mineral oil, lubricating oil, grease, wax, asphalt and tar. (4)(5)
Diesel oil is in a group called middle distillates, because the boiling point is about in the middle between the light fractions and the heavy products. These range from Kerosene to heating oil. Diesel is cheaper to refine than gasoline which contains many additives, and should be cheaper to buy. Diesel comes in two grades, ASTM #.1 and #.2. Most engines use #.2. No. 1 is used at lower temperature but does not have as much energy as #.2. The fuel is not much different from heating oil but because it is taxed,
heating oil and farm implement fuel is dyed a dark red to differentiate it. (6)

- Diesel fuel must be very clean. Small amounts of particulate mater or water can plug the fuel injectors. Storage can be a problem as bacteria can grow and foul the injectors. In the past diesel contained higher quantities of sulfur, now however the sulfur content has been reduced to 0.05%. This has affected the lubricity of the fuel requiring that additives be added to improve this property. Biodiesel is an effective lubricant when added to petrodiesel.
- Diesel fuel produces more greenhouse gasses than gasoline; however it has a 40% better fuel economy and therefore produces less pollution. (6)

WHAT IS BIODIESEL

- Biodiesel is a non-fossil fuel alternative to petrodiesel produced from biomass. It can be produced from vegetable oil or animal fats. Although biodiesel contains very different compounds than petroleum derived diesel, it has combustion properties very similar to the former including the energy content and cetane ratings (Ability to start cold) it is comparable to diesel #2. (6)
- Biodiesel is composed of a mixture of “ESTERS” that are the products of the reaction of fatty acids (FFAs) and triglycerides with an alcohol. The alcohol usually used is methanol (CH3OH) with a catalyst, usually sodium hydroxide (NaOH) lye.
- Fatty acids are organic acids derived from natural fats and vegetable oils. They are naturally produced by a biosynthesis process involving a coenzyme acetyl-CoA. These acids when combined with glycerin become triglycerides which make up most animal fats and vegetable oils.(7)
• **A note of caution about methanol**: Methanol is dangerous and should not be ingested or inhaled or allowed to contact the skin. It can cause blindness or death.

• An ester is a compound produced by the reaction of an organic acid (fatty acid) and an alcohol. This is equivalent to the reaction between an acid and a base in inorganic chemistry the product being a salt and water. In this case the salt is the ester and water is also produced. (8)

\[
\text{R--C-OH} + \text{CH}_3\text{OH} \rightarrow \text{R--C-OCH}_3 + \text{H}_2\text{O}.
\]

• Biodiesel can be blended with petrodiesel in any amount. Biodiesel can gel at a higher temperature than petrodiesel, blending in cold weather can solve this problem.

**THE ECOLOGY AND ECONOMICS OF BIOFUELS**

• Ecologically biofuels are produced from renewal and replaceable resources, whereas oil and coal, as resources, are not. As a means of replacing some of our reliance on these two sources of energy, biofuels may help, but there is more to this story. Economics and government policy have a large effect
• Biofuels can certainly reduce our dependence on foreign sources of energy.
• Using waste materials that would be thrown away, such as restaurant wastes and fats from slaughter houses to make biodiesel is a good source of alternate energy.
• Biodiesel produces more carbon dioxide than gasoline however a diesel engine uses less fuel than a gasoline engine and produces 40% less pollution. There is also less sulfur in biodiesel than in petrodiesel.
• Brazil produces ethanol from sugarcane and is energy neutral because the waste called “bagasse” is used as fuel to distill the alcohol.
• Ethanol is produced by fermentation and as produced is about 12% alcohol with the balance water. To be used as fuel the water must be removed which consumes a great deal of energy. As a result Brazil is mostly independent of imported fuel.
• Corn is used in The United States to produce ethanol. As much as one half of the corn crop will be used to make ethanol in 2007. This will effect the price of corn, most of which is used for cattle feed and sweetener instead of sugar because of cost. Food costs may be rising. (9 )
• Producing ethanol from corn requires 29% more fossil fuel than is produced. This is because the waste products are not useful as fuel and the high cost of fertilizer and pesticides needed for corn. (10 )
• Biodiesel produced from wastes is energy efficient, fuel produced from virgin soybeans which uses 27% more fossil fuel is not. (10 )
• This analysis includes all the energy to go from seed to finished product.
• The government is also involved by subsidizing ethanol production and taxing some other products as well as taxing imports that might compete with domestically produced fuels.
• The economics depend on the price of petroleum based fuels as well as the cost of the raw materials. Restaurant wastes may be free but there is a cost of collecting and cleaning the oils. As the production increases the demand for raw material will increase and the cost of the materials will increase with competition.

HOW IS BIODIESEL PRODUCED
• Biodiesel can be easily produced in any quantity from a liter to many gallons. The method depends on the raw material. Aside from water and dirt which must be removed prior to any processing, the production is either a one step or a two step process depending on the makeup of the raw material, not including washing, drying and separating the byproducts.
The starting material may consist of two types of compounds: free fatty acids and triglycerides. If the reaction is with FFAs it is called "Esterification". If the reaction is with triglycerides it is called "Transesterification".

The diagram below shows a commercial process that deals with both.

\[\text{Methanol} + \text{NaOH} \rightarrow \text{Transesterification} \rightarrow \text{Crude Biodiesel} \rightarrow \text{Washing} \rightarrow \text{Finished Biodiesel}\]

\[\text{Waste vegetable oil} \leq 2.5\% \text{ FFA} \rightarrow \text{Esterification} \rightarrow \text{Sulfuric acid + Methanol}\]

\[\text{Waste vegetable oil} > 2.5\% \text{ FFA} \rightarrow \text{Esterification} \rightarrow \text{Sulfuric acid + Methanol}\]

\[\text{Crude Biodiesel} \rightarrow \text{Glycerol} \rightarrow \text{Methanol Recovery}\]

Figure 3. Process flow for Biodiesel process.

There are many commercial plants around the world producing Biodiesel. If the feedstock is uniform then production is conducive to continuous operations, if not then a batch operation is preferred. There is one operation in Pittsburgh; however Capital Technologies is considering building a ten million dollar plant in conjunction with Carnegie Mellon using a solid catalyst. United Biodiesel is operating a 2 million gallon plant, and there is a proposed nonprofit installation by Steel City Biofuels to supply River Quest with fuel.

If the feed contains a substantial amount of free fatty acid (FFA) then if the catalyst is sodium hydroxide another reaction will take place and soap will be formed. To prevent this, an acid catalyst is used, sulfuric acid and the ester is formed.
After the FFAs are reacted then the second stage transesterification can proceed reacting with triglycerides with an alkali catalyst as shown below. The “R” stands for long chain carbon and hydrogen atoms sometimes called fatty acid chains.

The presence of soap from the FFA reaction complicates the biodiesel process as it hinders the separation of the biodiesel from the waste water and glycerin. The soap contaminates the waste water and increases the quantity of water necessary for cleaning the product. The glycerin must be recovered as it has value.

Methanol is used in excess and will be present in the products and needs to be recovered. Distillation is the usual method and the separation from water is easily accomplished.

If the operation is small for personal consumption, the quality of the finished product is up to the producer, however if it is to be sold there are ASTM standards that must be maintained as to residual methanol, glycerin, and unreacted triglycerides, etc.
SO HOW DO WE MAKE SOME BIODIESEL FOR A DEMONSTRATION?

- There are several published methods available on the internet. Two are Mike Pelly’s method and Aleks Kac’s Foolproof way (8,9). There are several companies offering equipment and technologies mostly for large installations. There are also offers for small scale equipment.
- Mike Pelly’s is the simplest single stage, however if FFAs are present in quantity it makes a lot of soap which not only represents loss but it slows the process making separation difficult.
- Kac’s method is two stages using acid in the first stage to react the FFAs then using alkali in the second to finish the process. It uses an excess of methanol which must be recovered. The equipment in both cases is the same. (12)
• Stainless steel or polypropylene should be used for the reactor and the methanol mixing tank. Stainless is preferred as it is easier to heat with a jacket or coils. The methanol/catalyst mixture is produced separately by adding the catalyst (H2SO4 or NaOH) to the methanol carefully.

\[ \text{CH}_3\text{OH} + \text{NaOH} \rightarrow \text{CH}_3\text{O-Na} + \text{H}_2\text{O} \]

The product in this case is sodium methoxide which must be handled just as with methanol.

• This mixture is added to the oil in the reactor. The oil should be at 130F and free of water. The reactor should ideally have a tight-fitting cover which will allow the excess methanol to be distilled directly as removal aids in separating water and glycerin. To accomplish this the reactor needs to be fitted with a condenser and a receiving vessel for the recovered methanol.

• The greatest time consumption is in settling and separating the water/glycerin mixture as the chart below shows. This can be shortened using a liquid/liquid centrifuge. The separation will also be cleaner. (13)

![Transesterification Biodiesel Time Chart](chart.png)

• After the glycerin/water mixture is removed the biodiesel must be washed with water with a small amount of either acetic (vinegar) or
phosphoric acid. The final product should be neutral or very slightly acidic.

- The product must then be dried. Biodiesel must be free of glycerin, catalyst. Unreacted oil/fat and water.
- There is a market for glycerin, however it must be cleaned of alkali and water to have any value. The more purified the glycerin is the better price that can be realized. (12)

**HOW DO WE DEAL WITH STUDENTS? WHAT CAN WE TEACH THEM?**

Most of the students will be taking either biology or chemistry and should pick up on the terms used. A discussion with them to see who is taking which subject will help. The biology students should be familiar with the enzyme and fatty acids (lipids). The chemistry students, although not taking organic chemistry, should understand the acid/base reaction.

- There are dangerous chemicals involved here although in small quantities. The total process takes too long for a class.
- Molecular models are inexpensive and could be used to show the structure and the reactions better than drawings. The students could use them to see how the chemistry works.
- Containers can be used to show the various stages in the operation.
- A large schematic drawing with either the samples or pictures describing the complete process can be displayed.
- The older students could do the titration to find the FFA content of some oil.
- When CBD builds a demonstration plant, students can tour and observe the operations.

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