Biodiesel Synthesis

Techniques
Infrared Spectroscopy

Green Principles
Renewable Feedstock
Catalysis
Design for Degradation

Introduction
The United States is the largest single consumer of fossil fuels in the world. Each year the U.S. consumes approximately 125 billion gallons of gasoline and 60 billion gallons of diesel fuel, with our consumption growing every year. While the bulk of gasoline is consumed in the automobile, the diesel engine is used for a wide variety of transportation from trucks to boats to trains. Diesel fuel is also consumed in the generation of electricity, including the diesel-electric train engine. This is the result of the historical development of the diesel engine. The diesel engine was invented in 1897 by Rudolf Diesel. Diesel carefully controlled the development of his technology and so the gasoline engine developed more quickly into an efficient engine, relegating the diesel engine to lower efficiency, large engine applications including ships and boats, trucks, and the diesel-electric train engine.

Today diesel cars are considered to be an efficient alternative to gasoline powered automobiles, getting better miles per gallon. As the Earth's petroleum resources continue to be reduced and as much of it is found in unstable parts of the world, the need for a reasonably priced, more environmentally friendly alternative increases. Biodiesel shows great promise as a readily available replacement for petroleum diesel and can be synthesized on an individual level or on an industrial scale.

The methods behind biodiesel synthesis have been known for quite a while. In recent years, however, there has been significant interest in the production of biodiesel from the waste oils of the food industry. Every year, fast food restaurants in the U.S. produce over 3 billion gallons of used cooking oil. Since many gallons of this used oil inevitably end up in landfills and sewers, the production of biodiesel from waste oil has the potential to significantly reduce environmental impact.

Greening the Chemistry
This laboratory experiment demonstrates three key green principles: the use of renewable feedstocks, catalysis, and design for degradation.

Petroleum has been the source of diesel fuel for a long time, however early diesel engines ran on vegetable oil. Today diesel vehicles need to be modified to burn vegetable oil as a fuel; however vegetable oil can be readily converted into biodiesel. Biodiesel can be produced from many different sources of plant oils. Used vegetable oil can only meet a small amount of the diesel fuel demand. Currently soy oil is the major available unused oil source, but many vegetable sources are available. These sources are renewable and the carbon dioxide produced from the burning of the biodiesel is recycled into the next crop through the carbon cycle.

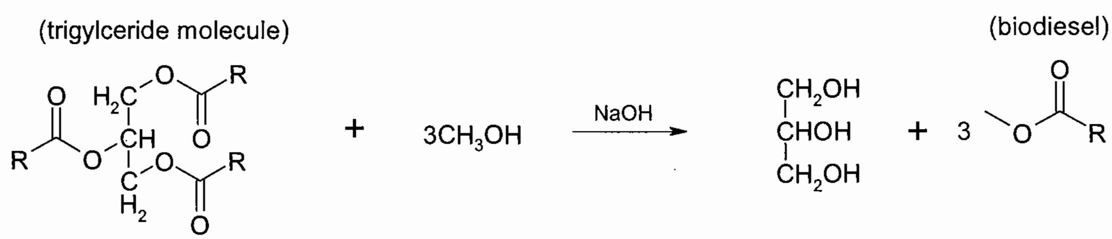
This reaction is catalyzed by NaOH, making this process economically viable for the industrial scale production of biodiesel. In the future biodiesel may also be made directly from lignocellulosic material (plant matter) as enzyme catalysts are being developed that can directly react with oils within the plant. Again the key is developing catalysts that can be used in an industrial setting.

Biodiesel is an excellent product as it is environmentally friendly. What is burned as fuel releases carbon into the biosphere that will be recaptured by growing plants. In effect, the biodiesel burned is reused in the next generation of crops that produces biodiesel, closing the loop rather than adding to global warming. The biodiesel that is spilled is not hazardous either. It is easily broken down as it is simply a modified natural oil.

Theory/Discussion

In this experiment you will synthesize diesel fuel from a triester of glycerol (a triacylglycerol or triglyceride). This reaction is known as a transesterification reaction. Transesterification is the process of transforming one type of ester into another type of ester. This reaction incorporates the use of the strong base sodium methoxide in a base-catalysed nucleophilic addition-elimination reaction at the carbonyl carbon of the triglyceride.

The reaction is a two step catalytic process. In the first step of the reaction, NaOH reacts with methanol in an acid-base reaction forming methoxide, a very strong base, and water. In the second step the sodium methoxide acts as a nucleophile and attacks a carbonyl carbon of the vegetable oil, forming a tetrahedral intermediate. In the final step the methyl ester separates from the glycerol backbone. This process is known as "cracking." The elimination of the glycerol backbone leads to the formation of the three methyl esters (the biodiesel) and glycerol. The NaOH is reproduced as a product in the reaction. If the biodiesel is removed from the mixture, glycerol and unreacted NaOH and methanol remain. The glycerine byproduct can be used as an additive to soap to make glycerine soap. The general reaction for forming biodiesel is shown below:



Experimental Procedure

(Note: The following procedure is for synthesizing a biodiesel mini-batch from 100% pure unused vegetable oil. This method can easily be modified for using recycled, used vegetable oil. Recycled vegetable oil must first be analyzed for free fatty acid and then a pH correction is made before following this procedure.)

1. Add 0.35 g of finely ground anhydrous NaOH into 20 mL of pure (99% or higher purity) methanol in a 250 mL Erlenmeyer flask containing a magnetic stir bar. Put the flask on a magnetic stir plate, and stir vigorously until all of the NaOH is dissolved. This flask now contains sodium methoxide. Note: Sodium methoxide is an extremely strong base and should be handled with care.

2. Warm up 100 mL of 100% pure vegetable oil to about 40°C in a 250 mL beaker. Warming the oil up is not necessary, but increases the reaction rate.

3. When all of the NaOH is dissolved, pour the 100 mL of oil into the methoxide solution while continually stirring. At first the mixture will become cloudy, but should soon separate into two layers. Stir for 15-30 minutes on high. (Stop here if experiment is being done over 2 weeks.)

4. Transfer the contents of the flask into a 250 mL separatory funnel. The mixture will separate into two different layers. The glycerol will fall to the bottom, and the methyl ester (biodiesel) will float to the top. Since about 75% of the separation occurs within the first hour, you will be able to see immediate progress. Allow the experiment to sit for about an hour.

5. Open the stopcock of the separatory funnel and allow the glycerol to drain into a small beaker. Make sure not to get any biodiesel in the glycerol or glycerol in the biodiesel.

6. Use the IR spectrometer to identify your products. Print out the spectras and compare with known spectra. The biodiesel may be hard to compare, since most oils are comprised of different length carbon chains. Comparing to known spectra can easily identify the glycerol. The presence of glycerol indicates a successful reaction.

Experiment Report

For this experiment I would like you to create a summary report. The report should be a typed one-page narrative and should include:

- ✓ A brief summary of your experiment and results
- ✓ Analyze the quality and error of your experiment.
- ✓ Evaluate this experiment in terms of its greenness.
    - o Give a brief overall analysis of the greenness of this reaction
    - o What recommendations do you have to improve the green character of this reaction?
- ✓ Attach a copy of your IR (another copy should be taped in your notebook).

Biodiesel Synthesis

Pre-laboratory Questions

1. Most oils and fats contain palmitic and stearic acid as building blocks. Give the structure for both these compounds.

2. Describe the role of sodium hydroxide in this reaction?

3. Complete the following tables of chemical data:

Compound	M.M. (g/mol)	Sol.	m.p. (°C)	b.p. (°C)	D (g/mL)
Sodium hydroxide			X	X	X
Methanol			X		
Glycerol			X		

4. Consider the chemicals used for this experiment. What realistic hazards are present? What safety procedures are necessary beyond wearing goggles and gloves?