Supplemental Material for On-line Publication

Biodiesel Synthesis and Evaluation. An Organic Chemistry Experiment

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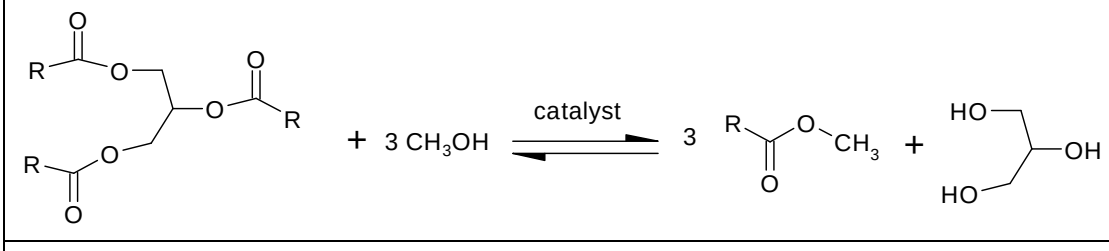
The supplementary material includes

1) Student Handout (Pages 2-18)
2) Notes for Instructor (Pages 19-23)
3) CAS Registry Numbers for All Materials (Page 24)

Synthesis and Evaluation of Alternative Fuels

The notion of using vegetable oil as a fuel source is as almost as old as the internal combustion engine itself. At the 1900 World's Fair in Paris, a Diesel engine, built by the French Otto Company, ran exclusively on peanut oil. Rudolf Diesel, inventor of the Diesel engine, originally did not foresee using vegetable oils for a fuel, but was impressed that the engine could run without modification on this agricultural fuel. Over time Diesel reflected on this achievement and in 1912 commented to the Institution of Mechanical Engineers (of Great Britain): "One cannot predict what part these oils will play in the Colonies of the future. In any case, they make it certain that motor-power can still be produced from the heat of the sun, which is always available for agricultural purposes, even when all our natural stores of solid and liquid fuels are exhausted."

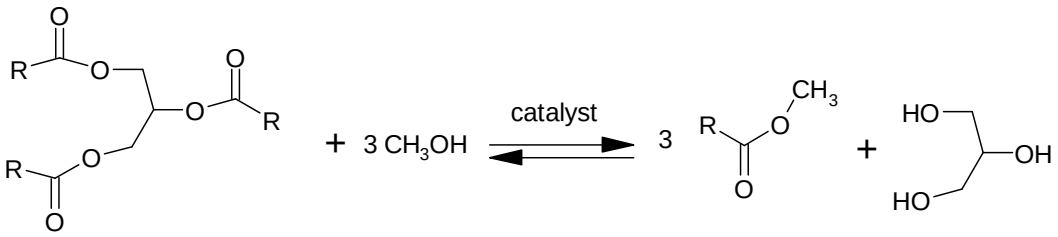
During the fuel and energy crisis of the 1970's and 1980's, a renewed interest in renewable fuels was sparked. Vegetable oil as a fuel itself was less viable as engine and fuel injector design had changed and could not utilize the viscous liquid. However, by transesterification reactions (see figure) the triacyglycerols of vegetable oils can be converted to a fuel with decreased viscosity compared to vegetable oils and fuel properties similar to diesel fuel. These ester derivatives are commonly known as biodiesel.



Triglyceride	Methanol	Methyl ester	Glycerol

The most common biodiesel fuels are derivatives of rapeseed or soy oil in the form of methyl esters, also known as fatty acid methyl esters (FAMEs). Ethanol has also been used to convert triglycerides to fatty acid ethyl esters (FAEEs), but separation of FAEE from glycerol is much more susceptible to a soap byproduct as excess ethanol can cause the formation of emulsions.

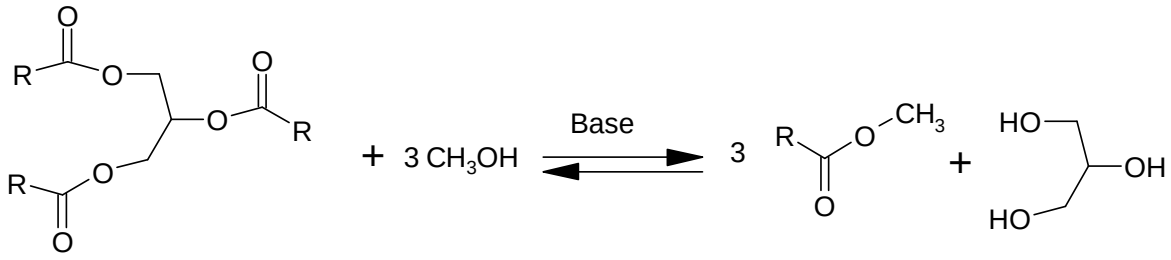
Transesterification/esterification reactions are equilibrium processes. Eventually the products and reactants form and react at a constant rate to produce a steady state.



$K_{acid\ catalyzed} = K_{base\ catalyzed}$

The equilibrium constant indicates whether a reaction is product or reactant favored, but does not imply how much time must pass to reach equilibrium. The equilibrium process takes longer depending on the rates of the forward and reverse reactions. Adding a catalyst does not affect the equilibrium, it only speeds up the attainment of equilibrium. Catalysts may either be basic or acidic materials.

Base catalyzed reactions can be completed with either alkaline metal hydroxides (sodium or potassium hydroxide) or alkaline metal alkoxides (sodium methoxide) :



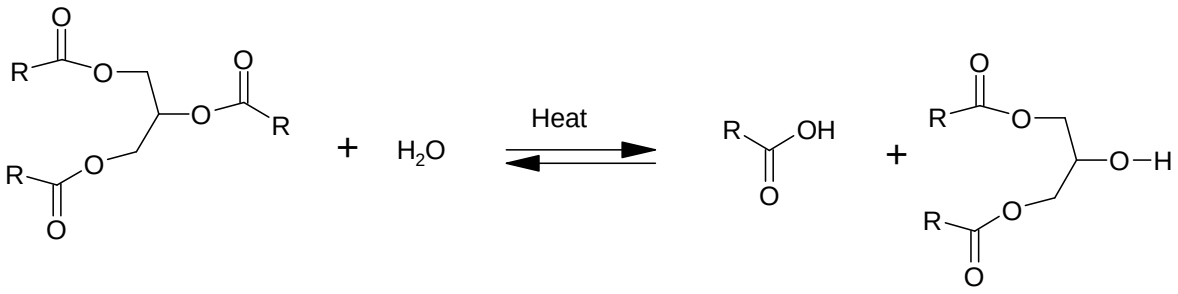
The alkaline metal hydroxide when dissolved in methanol forms sodium methoxide, which would be the same as adding sodium methoxide to methanol except that water is formed in the process.

$$NaOH + MeOH \longrightarrow NaOMe + HOH$$

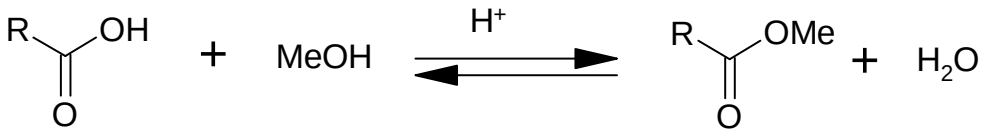
The reactions using the straight alkoxide in methanol give high yields (>98%) in as little as 30 minutes using 0.5 mol% of catalyst to starting triglyceride, whereas the metal hydroxides dissolved in methanol take somewhat longer (up to 4 hours, depending on reaction temperature) requiring 1-2 mol% of catalyst.

The reaction stoichiometry requires a 3:1 ratio of methanol:triglyceride, but a 6:1 mole ratio is used in practice. This is due to the equilibrium constant for this reaction having a value near unity (K=1). Le Chatelier's principle states that we can shift this equilibrium by applying heat, adding more reactant, or removing a product. Since it is difficult to remove product during this reaction, and heat does not affect the equilibrium much, the most effective way to shift the reaction forward is with excess reactant methanol.

Although acid catalysts can be used, they are generally avoided commercially as they result in much slower reaction times and require high methanol:triglyceride ratios of 20:1 and greater. One benefit, however, of acid catalyzed reactions is conversion of the free fatty acids found in waste vegetable oil to biodiesel.



As a vegetable oil is used to fry food, moisture (water) in the food combined with high heat tends to hydrolyze triglycerides to free fatty acids. These free fatty acids can account for up to 15% of the total weight of waste vegetable oil. In cases where free fatty acid content is greater than 1%, they can neutralize the base used in the transesterification reaction and result is poor yields of conversion. To solve this problem the waste vegetable oil is pretreated with an acid catalyzed (Fischer) esterification. The free fatty acids are converted to methyl esters, and the excess acid and water can be removed prior to base catalyzed transesterification.



In this lab you will act as a biodiesel producer. You have obtained waste vegetable oil stock to maximize the profit on your biodiesel production. Your goal is to create a marketable biodiesel. To be marketable you will need to prepare your biodiesel such that the end product has a minimum of free fatty acids, and glycerol which can cause carbon build-up in the pistons and fuel injectors of diesel engines. In order to maximize product, you will determine any free fatty acids and convert the acids to FAMEs via acid catalyzed Fischer esterification. Next you will convert any mono-, di- and triglycerides in the waste vegetable oil (WVO) to FAMEs by base catalyzed esterification. Finally, you will determine the completeness of the conversion product and quality of biodiesel by measuring the amount of free and bound glycerol in your final biodiesel product.

Experiment #1: Determination of Free Fatty Acid Content in Waste Vegetable Oil (WVO)

The feedstock that you will be using in this reaction is simulated waste vegetable frying oil (a mix of olive oil and oleic acid). As the oil is used in the fryer, some of the triglycerides in the oil are cleaved. This means that a small percentage of the original oil now exists as free fatty acids (FFAs) and glycerol. The small percentage of glycerol will not affect further reactions since it is an end-product in the transesterification process anyway. The free fatty acids, however, are problematic. The free fatty acids will neutralize any base that we are using to catalyze our reaction. We could use acid catalyzed esterification/transesterification to complete the entire reaction, but if this were a reaction that would be run at the 100's to 1,000's of gallon batch size, the amount of alcohol required to perform this reaction is uneconomical.

To alleviate the problem of FFAs in our feedstock for the reaction, we will determine the FFA content of the sample. Depending on the quality of the oil, free fatty acids can account for up to 15% of the total weight percentage of the oil. For base catalyzed reactions, the FFA content of the oil should be less than 0.5%. If our FFA content meets this requirement, we will proceed directly to the base catalyzed reaction. Should our FFA account for more, we will proceed with an acid catalyzed reaction.

Olive oil triglycerides contain a mix of fatty acids of varying chain lengths (oleic 73-84%, linoleic 10-12%, palmitic 9-10%, and stearic 2-3%), so we will only be able to approximate the percent of free fatty acid. Since olive oil is composed of roughly 75% oils of oleic acid, we will use this as our standard for determining weight percent of free fatty acids.

To determine free fatty acids, we will titrate a portion of our sample with a solution of 0.1 M potassium hydroxide. Since oleic acid is a weak acid, the pH of our titrated sample will be greater than 7, and we can use phenolphthalein as our indicator.

Procedure

1) Obtain a 50 mL buret.
2) Obtain 2 250-mL erlenmeyer flasks.
3) Clean your buret and fill it with 0.1 M KOH solution.
4) Add 2 ml of phenolphthalein solution to 75 ml of isopropyl alcohol in a 250 mL Erlenmeyer flask. This will serve as your solvent mixture.
5) With constant stirring titrate the solvent mixture with 0.1 M KOH solution to the first permanent pink color.
6) Weigh out 15 ± 0.02 g of sample oil into a second 250 mL Erlenmeyer flask.
7) Add the neutralized solvent mixture to the oil.
8) With contant stirring titrate the sample with 0.1 M KOH solution to the first permanent pink color of the same intensity as that of the neutralized sample.
9) Repeat steps 4-8 for a second sample of oil.

Results

Sample	1	2
Initial buret reading for titration of solvent		
Final buret reading for titration of solvent		
Volume of standardized KOH for neutralization of solvent (mL)		
Weight of oil sample (g)		
Initial buret reading for titration of oil in solvent mixture		
Final buret reading for titration of oil in solvent mixture		
Volume of standardized KOH for neutralization of oil in solvent (mL)		

Calculations

Percent Free Fatty Oleic Acid = $\frac{\text{\# of moles of FFA x molecular weight of oleic acid x100\%}}{\text{Weight of oil sample in grams}}$

$$\%FFA = \frac{[A - B][M][MW]}{[W]} * 100\%$$

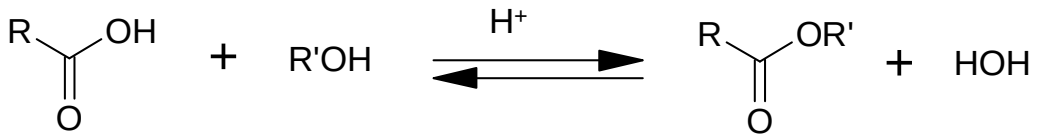
Where
A= L of KOH to titrate oil sample
B= L of KOH to titrate solvent
M= normality of KOH solution
MW= molecular weight of oleic acid (282.47 g/mol)
W= mass of sample titrated

Determined % free fatty acid as oleic in sample #1= _____
Determined % free fatty acid as oleic in sample #2= _____

Average % free fatty acid in WVO _____

Experiment #2: Acid Catalyzed Esterification of Free Fatty Acids in WVO

After you have determined the percent free fatty acid in your sample, you will complete the first part of our biodiesel reaction: acid-catalyzed esterification or sometimes called Fischer esterification. When a carboxylic acid is treated with a large excess of an alcohol in the presence of a strong acid catalyst, an ester is formed.



Since we are interested in forming fatty acid methyl esters we will use methanol as our alcohol and sulfuric acid as our catalyst.

The main consideration for this reaction is that for most primary alcohols, the equilibrium constant is near unity. To improve the formation of products, we will be using a 40:1 molar ratio of methanol to fatty acid in our waste vegetable oil sample.

Since you have determined the percent FFA in your WVO sample, you can now apply the following procedure to determine the methanol and sulfuric acid.

1) Weigh out approximately 45 g of WVO into a 100 mL round bottom flask (RBF).

2) From the weight of oil in the RBF and the % FFA determined in Experiment 1, determine the weight of FFA in your flask.

3) Take the weight of FFA and multiply by 5% (0.05) to determine the volume of concentrated sulfuric acid to use as a catalyst.

4) Using the molecular weight for oleic acid (282.47 g/mol) determine the approximate number of moles of FFA in the sample.

5) Using a 40:1 mole ratio of methanol:FFA, determine the volume of methanol to add. (density of MeOH=0.789 g/ml).

Pre-experiment calculations

Weight of sample for reaction(g)	
Percent FFA in sample for reaction	
Weight of FFA in sample	
Volume of Conc. H_2SO_4 catalyst	
Moles of FFA in sample	
Moles of methanol required for reaction	
Weight of methanol to add	
Volume of methanol to add	

Procedure

Mix the determined amount of acid to your determined amount of methanol. To a 100 mL round bottom flask add your waste vegetable oil with a stir bar. Place a reflux condenser on your flask and heat to about 40°C to decrease oil viscosity. Add your methanol/acid catalyst. Heat to about 60°C with a thermowell or heating mantle. Stir for 1 hour. Check frequently to ensure that the methanol and oil is mixed thoroughly. After 1 hour, decant the reaction mixture into centrifuge tubes. Centrifuge the tubes for 3 minutes at 2500 RPM. This will act to separate the methanol, acid catalyst, any glycerol and water formed which will act to hinder the following base catalyzed esterification. Your biodiesel layer will be the layer of higher density. After

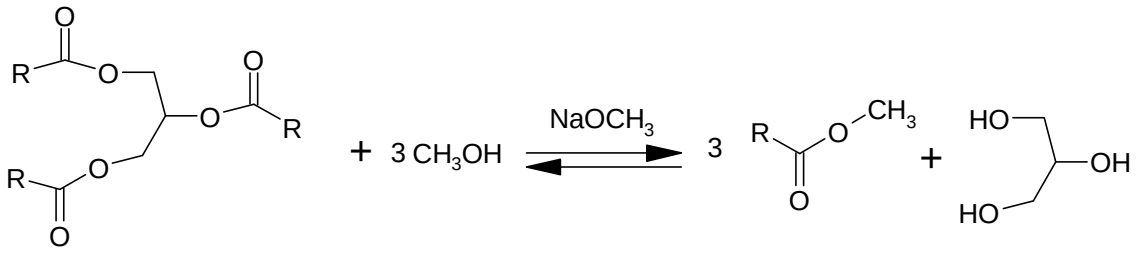
separation combine your FAME/oil layers, weigh the sample, determine the volume and place into your now cleaned round bottom flask. Proceed to the next experiment.

Data

Weight of combined biodiesel/oil layer (g)	
Volume of combined biodiesel/oil layer (mL)	

Experiment #3: Base Catalyzed Transesterification of WVO

After you have converted any free fatty acids to esters, you will complete the second part of our biodiesel reaction: base-catalyzed transesterification. When a triglyceride is treated with an excess of an alcohol in the presence of a strong base catalyst, a fatty acid methyl ester and glycerol are formed.



Since we are interested in forming fatty acid methyl esters we will use methanol as our alcohol and sodium methoxide as our catalyst. In the industrial setting, it is more cost effective to dissolve sodium hydroxide or potassium hydroxide into methanol. However, this leads to the formation of water that can decrease yields by converting some of the esters formed to their respective fatty acid. We will be using a 25% sodium methoxide in methanol solution as our catalyst to minimize the effect of water on our product. Manufacturers in Europe are moving towards using sodium methoxide instead of metal hydroxides for exactly the same reasons.

In this reaction, water will not affect the equilibrium process as much as the acid catalyzed esterification. In base catalyzed esterification, we will be using a 6:1 molar ratio of methanol to triglyceride in our waste vegetable oil sample to help shift the equilibrium forward.

In the previous experiment you have determined the volume of WVO/biodiesel after acid catalyzed esterification of free fatty acids. For a roughly 6:1 molar ratio of methanol to oil at this

point, a simplified approach can be used. Add methanol as 20% of the total volume of oil. So for a 100 gallon reaction, 20 gallons of methanol are required.

The amount of catalyst required depends on the nature of the catalyst. If sodium hydroxide or potassium hydroxide are used, the amount required is about 1-1.5% W/W oil. Since we will be using a more effective catalyst, sodium methoxide in methanol, we will only need a 0.5% W/W oil concentration. The sodium methoxide solution we are using is 25% W/W methanol. That is for 100 g of solution, 25 g are sodium methoxide.

Pre-experiment calculations

Weight of oil to convert (g)	
Volume of oil to convert (mL)	
Volume of methanol for reaction (mL)	
Sodium methoxide required for reaction (g)	
Volume of sodium methoxide solution to add to reaction (mL)	

Procedure

Mix your determined amounts of base catalyst and methanol. To a 100 mL round bottom flask add your acid treated waste vegetable oil and methanol with base catalyst. Heat the flask to 60°C and stir to ensure complete mixing for 20 minutes. After 20 minutes, cool and decant the reaction mixture into centrifuge tubes. Centrifuge the tubes for 10 minutes at 3500 RPM. This will act to separate any glycerol and water formed from the biodiesel product.

In the next experiment, you will determine the extent to which transesterification completed by measuring the amount of glycerol remaining in your biodiesel in the form of mono-, di-, and triglycerides.

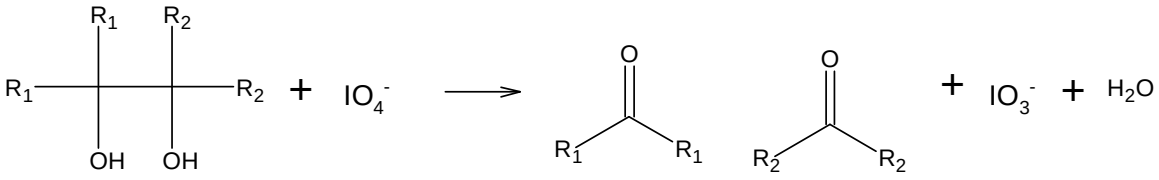
Data

Final volume of biodiesel	
Final weight of biodiesel	
Density of biodiesel	

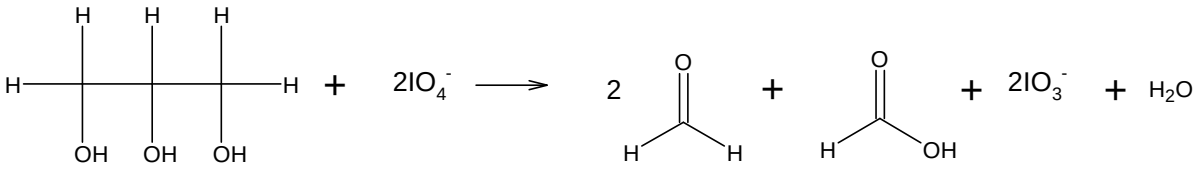
Experiment #4: Analysis of Free, Total and Combined Glycerol in WVO Biodiesel Product

This experiment is performed to analyze total, free and combined glycerol (as mono-, di-, and triglycerides) in your final product. The total glycerol is determined after saponification of the sample, the free glycerol directly on your sample, and the combined glycerol is determined by the difference. Because the product is a mixture of methyl esters of varying chain length, you will not be able to determine the mole percent of total or combined glycerol. Therefore glycerol is reported as weight percent of the biodiesel product. The ASTM standard for commercial biodiesel states that total glycerol by weight in the final product must be less than 0.25 % and the free glycerol be less than 0.02%. By determining the weight of glycerol in a specific weight sample of product biodiesel, we can determine if our product meets ASTM total glycerol specifications for marketable biodiesel.

Periodic acid oxidation of vicinal alcohols results in production of two carbonyl compounds, iodate and water:



When a compound contains three contiguous hydroxyl groups, two moles of periodic acid are consumed and the central carbon is oxidized to a molecule of formic acid. In the case of glycerol, two moles of formaldehyde, one mole of formic acid, two moles of iodate and one mole of water.



If a known excess of periodate is added to an unknown amount of glycerol, we can determine the quantity of glycerol by evaluating the molar excess of periodate after the reaction. This is accomplished by iodometric titration. By adding excess iodide to iodate, trioidide anion is formed:

$IO_4^- + 3I^- + 2H^+$ à $I_3^- + IO_3^- + H_2O$

The analysis of excess periodate will be accomplished by determining how much triiodide ion is produced. This is a routine procedure in which a solution of triiodide is titrated with a solution of sodium thiosulfate:

$I_3^- + 2\ S_2O_3^{2-}$ à $3\ I^- + S_4O_6^{2-}$

Therefore the net reaction is

$2\ S_2O_3^{2-} + IO_4^- + 2H^+$ à $IO_3^- + S_4O_6^{2-} + H_2O$

or two moles of thiosulfate reacts with one mole of periodate. We have now been able to determine the moles of periodate remaining after reaction. This is the number of moles of periodate not reacting with glycerol. From the total number of moles added to the product mixture, subtracting the moles reacting with thiosulfate, we can determine the total numbers of moles periodate reacted with glycerol. Finally, recognizing that the reaction of glycerol with periodate is in a two mole glycerol to one mole of iodate, we can determine the moles of glycerol in the sample. From molecular weight of glycerol, we can determine the weight percent of glycerol in the product sample analyzed.

Procedure

Dilution to obtain free glycerol

Add 5.000 g (precision to three decimal places) of your FAME into a 100 mL volumetric flask. Add 9.0 mL of dichloromethane. Add approximately 50 mL of water, stopper and shake vigorously for 60 seconds (be sure to vent). Add distilled water to bring the total volume to 100 mL and mix again by gently inverting the flask. Set the flask aside until the organic and aqueous layers separate.

Saponification to obtain total glycerol

Add 5.000 g (precision to 3 decimal places) of your FAME into a 50 mL round bottom followed by 15 mL of 0.7 M KOH in 95% ethanol. Reflux this mixture for 30 minutes. In a separate 125 mL separatory funnel, add 9.0 mL of dichloromethane and 2.5 mL of glacial acetic acid. Wash down the reflux condenser with 5 ml of distilled water, and transfer quantitatively to the volumetric flask using approximately 50 mL of distilled water. Shake vigorously for 60 seconds. Add distilled water to bring the total volume to 100 mL and mix again by gently inverting the flask. Set the flask aside until the organic and aqueous layers separate.

Determination of glycerol in dilute sample

1) Pipet 25 mL of periodic acid reagent into 6- 250 mL Erlenmeyer flasks.
2) Add 25 mL of distilled water to the first two flasks as blanks.
3) Pipet 25 mL of the aqueous layer representing total glycerol into 2 of the beakers containing periodic acid
4) Pipet 25 mL of the aqueous layer representing free glycerol into 2 of the beakers containing periodic acid
5) Mix each container thoroughly, cover with a watch glass and let stand for 30 minutes.
6) Add 10 mL of potassium iodide solution to the first blank solution and let stand for 60 seconds.
7) Dilute the sample to approximately 125 mL with distilled water and titrate with the standardized sodium thiosulfate solution. When the orange color has almost disappeared…
8) Add 2 mL of the starch indicator solution and continue the titration until the blue iodine starch color disappears.
9) Repeat steps 5-7 with each of the other flasks.

Calculations:

$$glycerol\% = \frac{[B - S][M][0.0230]}{[W] * 0.294} * 100\%$$

Where B= mLs of thiosulfate to titrate the blank
Where S= mLs of thiosulfate to titrate the sample
Where M= normality of thiosulfate
Where W= weight of sample extracted in g

Notes for Instructor:

Solutions required for glycerol analysis:

Periodic acid solution is 2.7 g of periodic acid in 100 mL of glacial acetic acid, dilute to 1.00 L with distilled water. Mix thoroughly. Store the solution in a dark glass-stoppered bottle, or in the dark in a clear glass stoppered bottle. Note: Only glass stoppered bottles can be used. Do not use cork or rubber stoppers under any circumstances as periodic acid is a strong oxidizer.

Thiosulfate solution (0.1 M) is 24.8 g sodium thiosulfate in 1.00 L distilled water. This can be standardardized any number of ways, however for the organic lab I do not standardize.

Potassium iodide solution (0.9 M) is 150 g diluted to 1.00 L.

Starch indicator is 10 g of soluble starch in cold distilled water to make a paste. To the paste add 1 liter of rapidly boiling water, stir rapidly for a few seconds and cool. Salicylic acid (1.25 g per liter) can be added as a preservative. Store the solution in a refrigerator when not in use. Fresh indicator must be prepared when the end point of the titration fails to be sharp. A sensitivity test can be administered by placing 2 mL of the solution in 100 mL of distilled water and add 0.05 mL of 0.1 M iodine solution. The deep blue color produced must be discharged by equivalent volume of 0.1M thiosulfate solution.

Alcoholic KOH is 39.277 g of KOH in 1.00 L of 95% ethanol. Filter if solution is cloudy.

Experiment 1 Comments:

While olive oil is too expensive as a commercial starting material for biodiesel, its use in the lab simplifies factors in FFA analysis. Olive oil contains up to 85% oleic acid naturally, so any FFA before spiking is predominantly oleic acid. The determination of FFA is completed using a modification of AOCS Official Method Cd 3a-63. Acid Value.[1] This method requires toluene, which we determined does not need to be present as a solvent in the analysis. Analysis on the purchased oil before spiking indicated a 0.22% level of FFA using the modified AOCS method. Communications with the olive oil manufacturer confirmed these findings as their lot analysis on the oil purchased was also 0.22% free oleic acid. To save time, the students can also be given the percent free fatty acid in the sample, as this first part of the lab takes about an hour as students need to refresh their memory on titrations from general chemistry. An alternative is to have the students determine the percent FFA in the sample after acid catalyzed esterification. We have also successfully used isopropyl alcohol purchased at a drug store in this titration.

Experiment 2 Comments:

During this reaction and the base catalyzed reaction, be sure that the methanol and oil is well stirred to make the mixture as homogenous as possible. Since the methanol does not dissolve in the oil, complete conversion may not occur. In cases where stirring is incomplete, the product after an hour will result in a cloudy bottom layer that contains oil, a small amount of biodiesel and FFA. After centrifugation, the methanol and acid catalyst can still be removed, however, the FFA in the oil will neutralize the base catalyst in the next step. The result will be an incomplete conversion of oil to biodiesel. Prior to the experiment, 3Å molecular sieves are placed in the methanol to ensure dryness.

Experiment 3 Comments:

Sodium hydroxide dissolved in methanol can be used instead of sodium methoxide. The amount of catalyst required is 1-1.5% W/W of oil. Reaction times will also need to be lengthened somewhat to obtain the percent conversion using sodium methoxide.

If the student had FFA present in the oil obtained from experiment 2, the resulting product will appear as a very small top layer of biodiesel and a large bottom layer of unconverted oil, FFA, glycerol and some biodiesel. The large amount of oil in the sample will be outside of the detection limits of the glycerol analysis in Experiment 4.

Experiment 4 Comments:

After saponification to obtain total glycerol, we use a wash bottle to squirt approximately 5mL of water down the reflux column. When shaking the 100mL volumetric flask, do not use Parafilm to seal the top as the dichloromethane dissolves it. We use rubber stoppers instead. For addition of starch indicator, we wait until the brown solution has become orange and not yellow to ensure that the student has a clear endpoint and does not miss it.

The determination of total, free and combined glycerol in the final biodiesel sample is completed utilizing a modification of American Oil Chemists' Society Method Ca 14-56 Total, Free and Combined Glycerol (Iodometric-Periodic Acid Method)[2] by oxidation of glycerol with periodic acid and subsequent periodate titration. In this method, glycerol reduces periodate to iodate; the iodate in turn, and any remaining periodate, is ultimately determined iodometrically by reaction with thiosulfate. Thus, the decrease in the amount of thiosulfate required, when compared to a blank containing the same initial amount of periodate, gives a measure of the amount of glycerol present.

In the official method when determining free glycerol, a 10 g sample of FAME is dissolved in 90 mL of chloroform and diluted to 1 L with water. The first modification to the method is to use a 5 g sample, add nine mL of dichloromethane and dilute to 100 mL. By decreasing volumes, the amount of chlorinated solvents used in lab is limited. The second modification is in the periodic acid reactant solution. The original solution is 5.4 g of periodic acid in 100 mL of water and 900 mL of glacial acetic acid. The modification is to add 2.7 g of periodic acid in 100 mL of glacial acetic acid and dilute to 1 L with distilled water. This second modification makes the procedure more economical and eliminates generation of large volumes of acetic acid waste.

Run	Method of Extraction	Biodiesel Sample size (g)	H_5IO_6 reactant volume and preparation	Volume of sample to added to the H_5IO_6 reactant (mL)	% glycerol found (w/w)
1	AOCS	10.014	50.0mL of 0.1M in acetic acid	50.0	2.56 ± 0.02
2	Modification	5.028	50.0mL of 0.1M in acetic acid	25.0	2.49 ± 0.02
3	AOCS	10.014	10.0mL of 0.1M in acetic acid	10.0	2.66 ± 0.07
4	Modification	5.019	10.0mL of 0.1M in acetic acid	10.0	0.931 ± 0.006
5	AOCS	10.014	25.0mL of 0.1M in 1.75M acetic acid	25.0	2.50 ± 0.01

Table 1: Analysis of glycerol in the same biodiesel sample by AOCS and modified AOCS methods.

As shown in Table 1, analysis of glycerol in samples prepared by the original method and the new method do not differ greatly when analysis is performed as prescribed in the original AOCS

Method (Run 1 and 2). To see if decreasing the volume of the original periodic acid reactant volume, a 10.0 mL aliquot was used (Run 3 and 4). While the percent glycerol by weight does not change dramatically as compared to the standard method, the modification resulted in a significantly different value. This is most likely due to the titration volume of thiosulfate solution required for the blank versus the sample. According to the AOCS method, the volume of thiosulfate solution titrated for the sample must be at least 80% of the blank. In the case of the modification, since the concentration of glycerol in the aqueous sample is much greater, the amount of thiosulfate required for titration is much less than the 80% required. Finally, when using a periodic acid solution that is 0.1 M in 100 mL of acetic acid diluted to 1.00 L with water, the results are nearly identical as when the periodic acid is dissolved in glacial acetic acid (Run 5).

Instructor Notes References

1) AOCS Official Method Cd 3a-63. Acid Value. In Methods and Recommended Practices of the American Oil Chemists' Society, AOCS Press, Champaign, IL 1997
2) AOCS Official test Method Ca 14-56. Total, Free and Combined Glycerol (Iodometric-Periodic Acid Method). In Methods and Recommended Practices of the American Oil Chemists' Society,AOCS Press, Champaign, IL 1991

Chemicals Required for Complete Experiment

Name	CAS#
2-propanol (isopropyl alcohol) 70% in water	67-63-0
Potassium hydroxide	1310-58-3
Phenolphthalein	77-09-8
Oleic acid	112-80-1
Sulfuric acid	7664-93-9
Methanol	67-56-1
Sodium Methoxide	124-41-4
Periodic acid	10450-60-9
95% Ethanol	64-17-5
Dichloromethane	75-09-2
Sodium thiosulfate	7772-98-7
Acetic acid	64-19-7
Soluble starch	9005-84-9
Salicylic acid	69-72-7