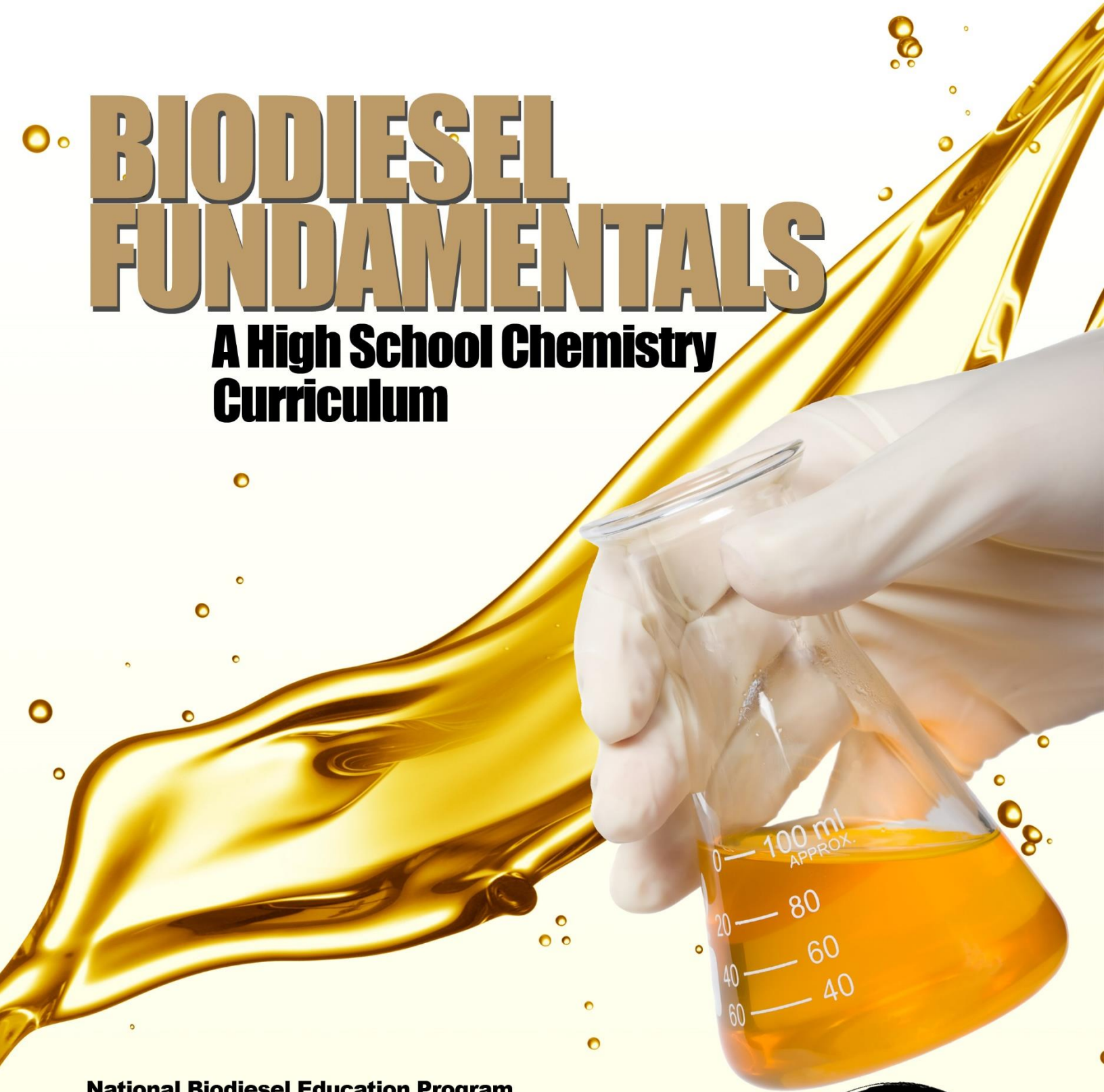


# BIODIESEL FUNDAMENTALS

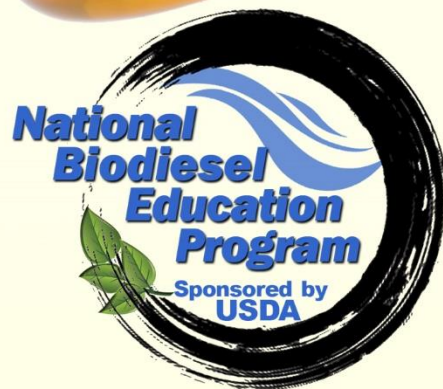
## A High School Chemistry Curriculum



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## Notes to the Instructor

These labs are designed to be used during the second semester of a standard high school chemistry class. We hope to show students how chemistry principles can be used in the real-world industry of biodiesel production.

While each lab can stand on its own, each also builds on the previous labs, so using them in sequence can provide a richer experience.

Each lab can be photocopied and handed out to students.

Here are additional notes, instructions, and tips.

### Lab 1: The Molecules of the Biodiesel Reaction

#### Content Standards of High School Chemistry – Major Objectives

- Students will distinguish and classify matter into appropriate categories (Idaho content standard 11-12-C.2.1.4)
- Students will correctly write symbols, formulas, and names for common elements, ions, and compounds (Idaho content standard 11-12-C.1.8.1)

### Lab 2: Chemical Reactions

#### Content Standards of High School Chemistry – Major Objectives

- Students will use the periodic table to predict physical and chemical properties (Idaho content standard 11-12-C.1.1.1)
- Students will perform calculations related to the conversion of grams to moles to particles, atoms, molecules and volume (Idaho content standard 11-12-C.1.3.4)
- Students will correctly write symbols, formulas and names for common elements, ions and compounds (Idaho content standard 11-12-C.1.8.1)

#### Calculating the molecular weight of calcium chloride:

*Calcium chloride,  $\text{CaCl}_2$  has 1 calcium atom and 2 chlorine atoms. The atomic weight of Ca is 40.078 and Cl is 35.453. Therefore:*

ATOM	NUMBER	ATOMIC WEIGHT Of the ATOM	TOTAL WEIGHT
Ca	1	40.078	40.078
Cl	2	35.453	<u>70.906</u>
			110.984

Since we do not need to use this much reactant to demonstrate this chemical reaction, divide the molecular weight of calcium chloride and the molecular weight of sodium carbonate by 10. One-tenth the molecular weight calcium chloride is 11.1.

The students will then weigh out 11.1 grams of calcium chloride,  $\text{CaCl}_2$  and pour this into the flask with the  $\text{CaCl}_2$  label.

## Calculating the molecular weight of sodium carbonate:

Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) has 2 sodium atoms, 1 carbon atom, and 3 oxygen atoms. The atomic weight of Na is 22.990, C is 12.011, and O is 15.999. Therefore:

ATOM	NUMBER	ATOMIC WEIGHT Of the ATOM	TOTAL WEIGHT
Na	2	22.990	45.980
C	1	12.011	12.011
O	3	15.999	<u>47.997</u>
			105.988

One-tenth the molecular weight of sodium carbonate is 10.6.

The students will then weigh out 10.6 grams of sodium carbonate,  $\text{Na}_2\text{CO}_3$ , and pour this into the flask with the  $\text{Na}_2\text{CO}_3$  label. Attach the stopper and shake until all the  $\text{Na}_2\text{CO}_3$  is in solution. There may be some cloudiness in one of the test beakers at the end of the lab. This could be from impurities in the reagents, such as moisture.

## Lab 3: Acid Values of Vegetable Oils via Titration

### Content Standards of High School Chemistry – Major Objectives

- Students will distinguish the common theories defining acids and bases (Idaho Content Standard 11-12-C.1.2.4)
- Students will analyze quantitative relationships involved in acid/base chemistry including pH (Idaho Content Standard 11-12-C.1.3.8)

### Potassium hydroxide-isopropyl alcohol solution, 0.1 N (the titrant)

Instructor should prepare by adding 6 g of potassium hydroxide to approximately 1 L of isopropyl alcohol, then accurately determine the exact concentration to 0.002N by titration using a known concentration of standard acid solution.

### Titration solvent

Instructor should prepare by adding 5 mL distilled water to 495 mL of anhydrous isopropyl alcohol to one (1) liter of the solution, and then adding 500 mL toluene.

## Lab 4: Chemical Equilibrium in Biodiesel Production

### Content Standards of High School Chemistry -- Major Objectives

- Students will analyze and solve reaction stoichiometry problems (Idaho content standards 11-12-C.1.3.5)
- Students will correctly write symbols, formulas and names for common fatty acids and other compounds (Idaho content standards 11-12-C.1.8.1)
- Students will communicate scientific investigations and information clearly (Idaho content standards 11-12-C.1.8.2)

In this lab students will make a small batch of biodiesel in two stages. The instructions call for allowing the oil and alcohol mixture to sit for 60 minutes, in order to allow time for the reaction. If needed, it is fine to have the mixture sit for longer than 60 minutes (for example, overnight or over the weekend) if you need to continue the lab on another day.

## Lab 5: Transesterification of Vegetable Oil and Alcohol to Produce Ethyl Esters (Biodiesel)

### Content Standards of High School Chemistry – Major Objectives

- Students will demonstrate the conservation of matter by balancing chemical equations (Idaho content standard 11-12-C.2.3.2)
- Students will classify, write and balance chemical equations for common types of chemical reactions and predict the products (Idaho content standard 11-12-C.2.5.2)
- Students will describe the factors that influence the rates of chemical reactions (Idaho content standard 11-12-C.2.5.3)

In this lab students will make a small batch of biodiesel. The instructions call for allowing the oil and alcohol mixture to sit for 60 minutes, in order to allow time for the reaction. If needed, it is fine to have the mixture sit for longer than 60 minutes (for example, overnight or over the weekend) if you need to continue the lab on another day.

## Lab 6: Physical and Chemical Solubility

### Content Standards of High School Chemistry – Major Objectives

- Students will analyze and solve reaction stoichiometry problems (Idaho content standard 11-12-C.1.3.5)
- Students will express concentrations of solutions in various ways
- Students will explain the relationship and reactions of acids, bases, and salts (Idaho content standard 11-12-C.2.1.5)

This lab was adapted from these two labs:

- “Solubility of a Salt,” on the Center for Precollegiate Study at the University of Florida’s web site:  
<http://www.cpet.ufl.edu/bestpractices/PDF/Physical%20Science/Changes%20in%20Matter/Investigating%20the%20Solubility%20Of%20a%20Salt%20and%20the%20Effects%20Temperature%20has%20on%20it.pdf>
- “The Solubility of a Salt,” on Central School site (Saskatchewan Schools, Canada):  
[http://www.saskschools.ca/curr\\_content/chem30\\_05/4\\_solutions/labs/solubility\\_salt.pdf](http://www.saskschools.ca/curr_content/chem30_05/4_solutions/labs/solubility_salt.pdf)

## Lab 7: Using Differences in Solubility to Remove Contaminants from Biodiesel

### Content Standards of High School Chemistry – Major Objectives

- Students will express concentrations of solutions in various ways including molarity (Idaho content standard 11-12.C.1.3.6)
- Students will evaluate the role of chemistry in energy and environmental issues (Idaho content standard 11-12.C.5.3.1)

### 1 liter unwashed biodiesel

*Instructor should dissolve 2.5 g KOH in 50 mL methanol. Add this to 1 liter of unwashed biodiesel. This will ensure that there is enough catalyst to measure in the biodiesel sample. This solution should be prepared immediately before the class because over time the KOH will react with the biodiesel to produce soap.*

### 0.1 N Hydrochloric acid

*Instructor should purchase or prepare 0.1 N HCl solution. To prepare, dissolve 9.85 g of concentrated (37%) HCl in 1 liter of distilled water. Standardize by titration against a known standard of base.*

## Lab 8: Density Measurement of Chemicals and Fuels

### Content Standards of High School Chemistry – Major Objectives

- Students will create and interpret graphs of data (Idaho Content Standard 11-12-C.1.2.2)
- Students will select and use appropriate scientific equipment, materials and techniques (Idaho Content Standard 11-12-C.1.6.2)
- Students will demonstrate the ability to work safely and effectively in a chemistry laboratory (Idaho Content Standard 11-12-C.5.1.1)

## Standard Lab Report Format

As the instructor, you may have your own laboratory report format. If not, here is a suggested format.

- a) Cover page, containing the title of the lab, to whom, from whom, and date.
- b) Objective(s) of the lab
- c) Methodology
  - c.1 Equipment/devices
  - c.2 Chemicals used, if any
  - c.3 Set-up
  - c.4 Procedures
- d) Data and Presentation
  - d.1 Phenomena observed
  - d.2 Raw data collected
  - d.3 Data processing/calculations
  - d.4 Data summary
- e) Results and Discussions
  - e.1 Observations
  - e.2 Concepts learned
  - e.3 Discussions
- f) Questions that remain/ newly raised

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## Safety Warnings

In some of these labs you will be working with toxic chemicals. When working with these chemicals, you must follow these rules:

- Everyone must wear safety glasses or goggles, and gloves, while working in the laboratory.
- Lab coats or aprons should be worn by those involved with pouring or mixing chemicals.
- If a fire occurs, leave the building immediately. Do not try to fight it!

The following dangerous chemicals are commonly used for biodiesel production:

- Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are dangerous chemicals. Please read the Material Safety Data Sheets before handling these hazardous chemicals. They can severely burn your skin on contact. If you get any in your eye, it can blind you. If you get any on your skin, the prescribed treatment is to flush with LOTS of water for up to 30 minutes. Always wear safety goggles when using NaOH and KOH.
- Methanol is highly toxic. It can easily enter the blood stream by breathing the vapors and by absorption through the skin. Methanol may cause liver damage, swelling of the retina of the eye, and brain damage or death in extreme cases. When making biodiesel, catalysts like potassium or sodium hydroxide are dissolved in methanol to form methoxides. These compounds in solution with methanol are even more toxic and corrosive.

In addition, some of these labs use other potential dangerous chemicals:

- Isopropyl alcohol is highly flammable.
- Ethanol is highly flammable.
- Toluene is highly flammable.
- Potassium nitrate can irritate the eyes, skin, and lungs (if inhaled).
- Petroleum diesel can cause skin irritation, and is poisonous.

## Facts About Biodiesel

### What is Biodiesel?

Biodiesel is a diesel fuel replacement made from vegetable oil or animal fat. It is not the same as ethanol, which is made from sugar or starch, and which is used in engines that run on gasoline. Biodiesel is used in engines that run on diesel fuel.

Commonly used feedstocks for the production of biodiesel include soybean oil, rapeseed/canola oil, used (waste) vegetable oils, and animal fat. Warm climate tree oils such as palm oil and jatropha are used to make biodiesel in some parts of the world.

Biodiesel is also not the same as straight vegetable oil or animal fat. A normal diesel engine will eventually be damaged through the use of straight vegetable oil or straight animal fat fuel. Vegetable oils or animal fats must be converted into biodiesel by reacting the oil or fat with an alcohol in the presence of a catalyst. This process is referred to as *transesterification*.

In chemical terms, biodiesel can be called *fatty acid methyl esters* when made with methanol or *fatty acid ethyl esters* when made with ethanol. These terms are often shortened to methyl esters and ethyl esters. Sometimes biodiesel is referred to as *alkyl esters*. This is a general term that includes biodiesel made with any alcohol.

### Is Using Biodiesel Good for the Environment?

Biodiesel produces 5.5 times more energy than the fossil energy used to produce it. This is a fantastic *energy balance*, and proves that biodiesel is a renewable fuel.

Using biodiesel can help reduce greenhouse gas emissions. Although burning biodiesel does release carbon dioxide (a major greenhouse gas) into the air, this carbon was first removed from the air by the plant feedstock. However, biodiesel is not carbon neutral, because the process of growing the feedstock generally uses some fossil fuels (such as fertilizer and tractor fuel).

Biodiesel produces less air pollution (exhaust emissions) when burned in an engine than diesel made from fossil fuels.

### How Much Biodiesel is Produced in the U.S.?

In 2011, over a billion gallons of biodiesel were produced in the United States. While this is an impressive number, it represents only 1/40 of the amount of the diesel fuel used in the U.S.

For more information about biodiesel, visit the biodiesel pages on eXtension:  
<http://www.extension.org/pages/28783/farm-energy-biodiesel-table-of-contents>

## Laboratory 1: The Molecules of the Biodiesel Reaction

### Topics Covered

- Organic molecules relevant to biodiesel and its production, including: hydrocarbons, fatty acids, alcohols, triglycerides, methyl esters, sodium/potassium hydroxides, sodium/potassium methoxides, and glycerol
- Categorization of chemicals, e.g., hydrocarbons, alcohols, esters
- 3-D configurations of fatty acids, methyl esters, and triglycerides

### Equipment Needed

- Molecule model building kits or household items that can be used to build the models (such as toothpicks and gumdrops). Use different colors of gumdrops to designate different atomic species.

### Background Information – Organic Chemistry

Organic chemistry is a science that deals with molecules and compounds that contain carbon. There are a vast number of gaseous, liquid, and solid substances that contain carbon. These are often energy sources like natural gas, propane, alcohol, gasoline, diesel fuel, biodiesel, coal, and biomass including wood.

When we talk about a “carbon footprint” we are referring to human activity that produces carbon dioxide ( $\text{CO}_2$ ) and thus contributes to climate change: things like burning fossil fuels for heat, electricity, and transportation. We can reduce our carbon footprint by using biofuels such as biodiesel and ethanol. Because these fuels are made from plants that absorb carbon from the atmosphere as they grow, biofuels add less new carbon dioxide to the atmosphere than do fossil fuels.

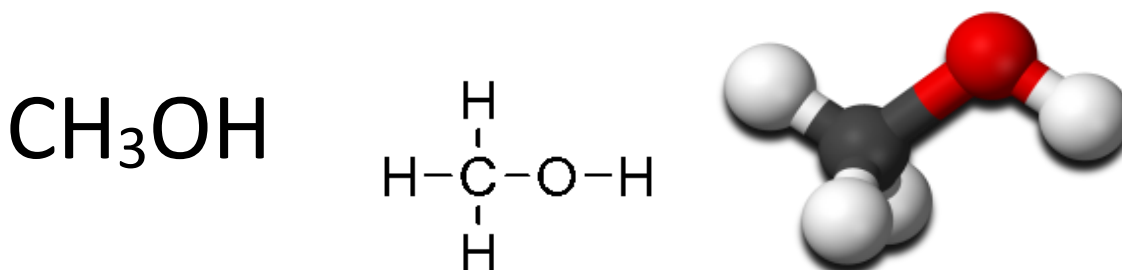
### Laboratory Procedure – Constructing the Molecules of Biodiesel Production

Biodiesel is made when a triglyceride molecule (oil or fat) reacts with 3 molecules of an alcohol (usually methanol or ethanol) to produce 3 molecules of biodiesel (also called “methyl esters” or “ethyl esters”) and one molecule of glycerol.

The structure of a molecule can be depicted using a chemical formula, a 2-dimensional structural chart, or a 3-dimensional model. In reality, all molecules are 3-dimensional, so we will be creating 3-dimensional models.

After you read the description and look at the models of each molecule, construct a model of that molecule using the molecule building kit, or other household items such as gumdrops and toothpicks.

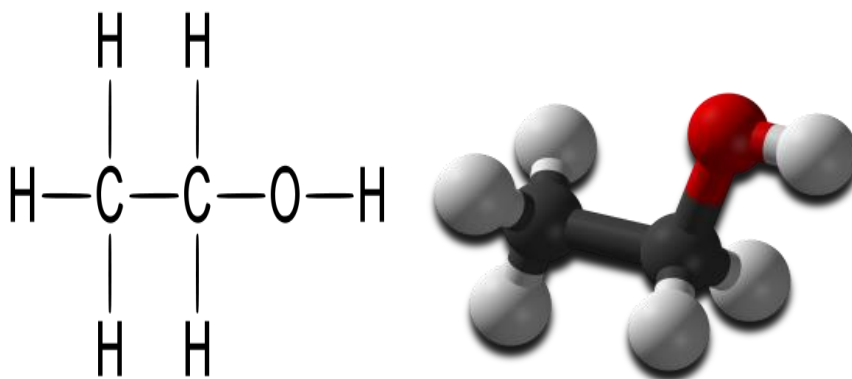
Methanol is the most commonly used alcohol in biodiesel production. It is the simplest alcohol with the formula  $\text{CH}_3\text{OH}$ , and is sometimes abbreviated  $\text{MeOH}$ . It is colorless and highly volatile. It is used in the manufacture of many consumer and industrial products and as a high octane fuel in racing engines.



**Figure 1** Here are three different ways of depicting the methanol molecule: a molecular formula, a structural formula, and a 3-D ball-and-stick model. Molecule models become more complex as additional details are revealed about the molecular structure.

**Exercise 1:** Construct a model of a methanol molecule.

Ethanol can also be used to make biodiesel. This type of alcohol is also called grain alcohol and is found in all alcoholic drinks. It can also be blended with gasoline as an octane booster and fuel extender for all gas-powered cars and trucks. Like methanol, it is also colorless and very volatile. It is a straight-chain hydrocarbon with a molecular formula  $\text{C}_2\text{H}_5\text{OH}$ , and is sometimes written  $\text{EtOH}$ .

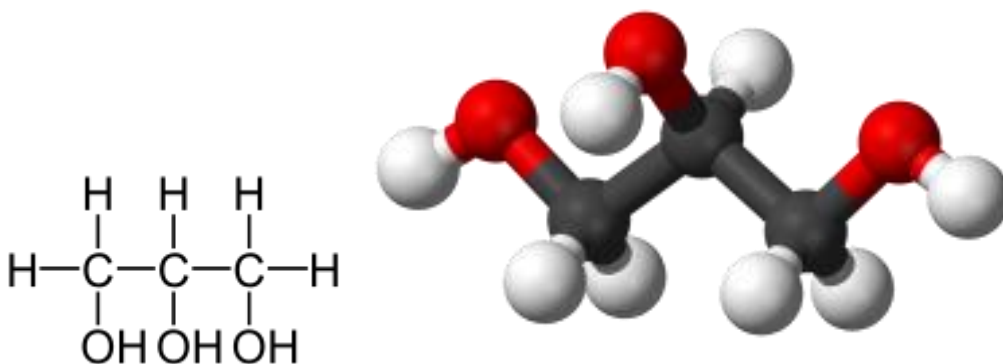


**Figure 2** Molecular structure and 3-D model of ethanol.

Notice the relatively larger size and weight of the ethanol compared to methanol, putting it at a disadvantage as a reactant for biodiesel, since a larger quantity is needed.

**Exercise 2:** Construct a model of an ethanol molecule.

Glycerol, also called glycerin or glycerine, is a ubiquitous substance found in almost all cosmetics, in many pharmaceuticals, in personal care products like shampoos, lotions, and toothpaste, and in a lot of food items. Natural or vegetable-based glycerol has the molecular formula  $C_3H_8O_3$  and forms the backbone of triglycerides (fats and oils). Glycerol is a byproduct of biodiesel production. It is also a byproduct of the soap-making process in which fats and oils are reacted with a strong base, forming sodium and/or potassium soaps, and releasing the glycerol.



*Figure 3 Glycerol structure*

Glycerol can also be made synthetically based on petroleum refining. Before the biodiesel industry began to flourish, synthetic glycerol had a large share of the market with a price advantage. However, presently there is an abundance of natural glycerol coming from biodiesel production that has reduced the price of natural glycerol.

### **Exercise 3: Construct a model of a glycerol molecule.**

Fatty Acids are part of triglycerides (fats and oils). In nature, they are made up of a chain consisting of an even number of carbons atoms from 4 to 28. Chains with an uneven number of carbons are much less common in nature.

Fatty acids are either saturated or unsaturated. Unsaturated fatty acids have double bonds between some of the carbons, whereas saturated fatty acids have no double bonds. Unsaturated fatty acids are generally classified as monounsaturated (they have one double bond), or polyunsaturated (they have two or more double bonds).

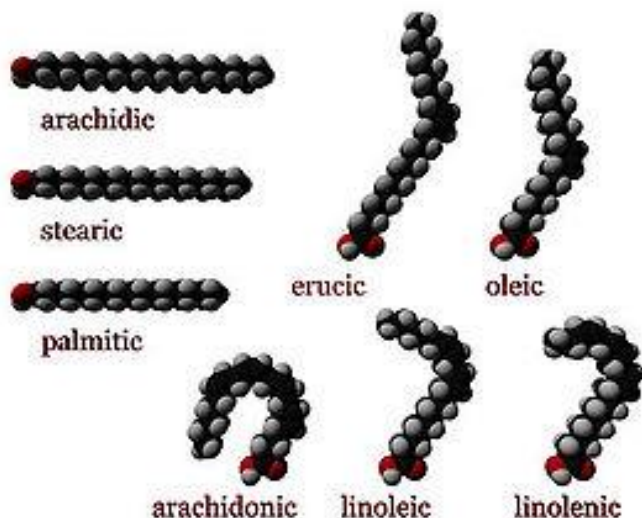
Fatty acids are often identified by name as well as by numbers in parentheses. The first number refers to the number of carbons, and the second number refers to the number of double bonds. Oleic acid (18:1) is a good example of a monounsaturated, with 18 carbons and one double bond.

Fatty acids have a carboxyl group ( $COOH$ ) at one end. It is this end that combines with the hydroxyl group ( $HO-$ ) on the glycerol molecule to form triglycerides.

Carbon atoms in a fatty acid are identified using the Greek alphabet, with the first carbon from the carboxyl group being labeled the alpha carbon, the next is the beta carbon, and so on. The last or terminal carbon is called the omega carbon. The most common form of linolenic acid (18:3) has three double bonds at 3, 6 and 9 carbons from the omega carbon. No doubt you have heard of Omega 3 and Omega 6 fatty acids as being essential in human nutrition. These names refer to the placement of the double bonds (counted from the last, or “omega,” carbon.)

Double bonds can occur in a cis or trans configuration. In the cis arrangement, adjacent hydrogen atoms are on the same side of the double bond. This form is commonly found in nature, and causes the chains to be bent or hook-shaped (in the case of multiple double bonds). In trans fatty acids, adjacent hydrogen atoms are on opposite sides of the double bond, causing the chain to be straighter and to act more like a saturated fatty acid.

Notice in figures 4 – 6 we show three ways of illustrating fatty acids: the first is the space-filling model, where the atoms are shown touching each other; the second is the familiar stick-and-ball model; and the third is simply the structural formula. Another way to depict a molecule such as a fatty acid is with a line drawing that does not show the individual carbon and hydrogen atoms in the chain, as in figure 6.



*Figure 4 Examples of different fatty acids*

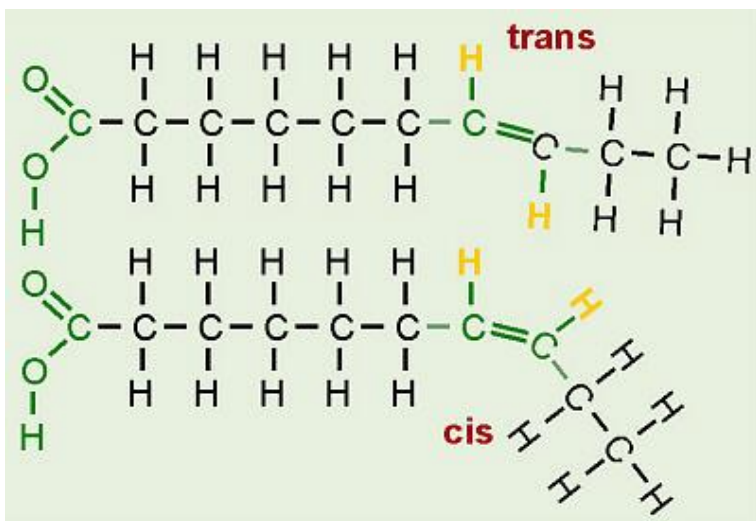


Figure 5 cis vs. trans configuration

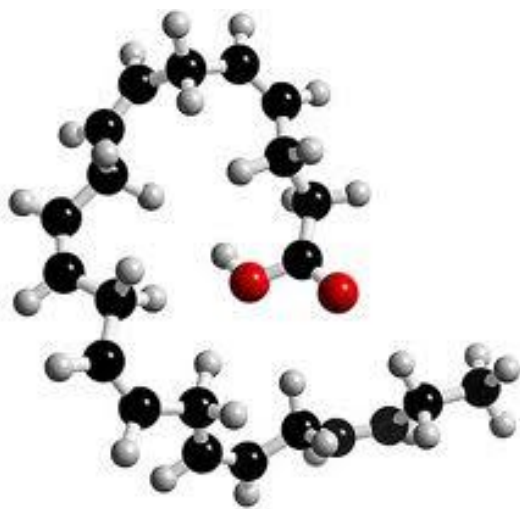
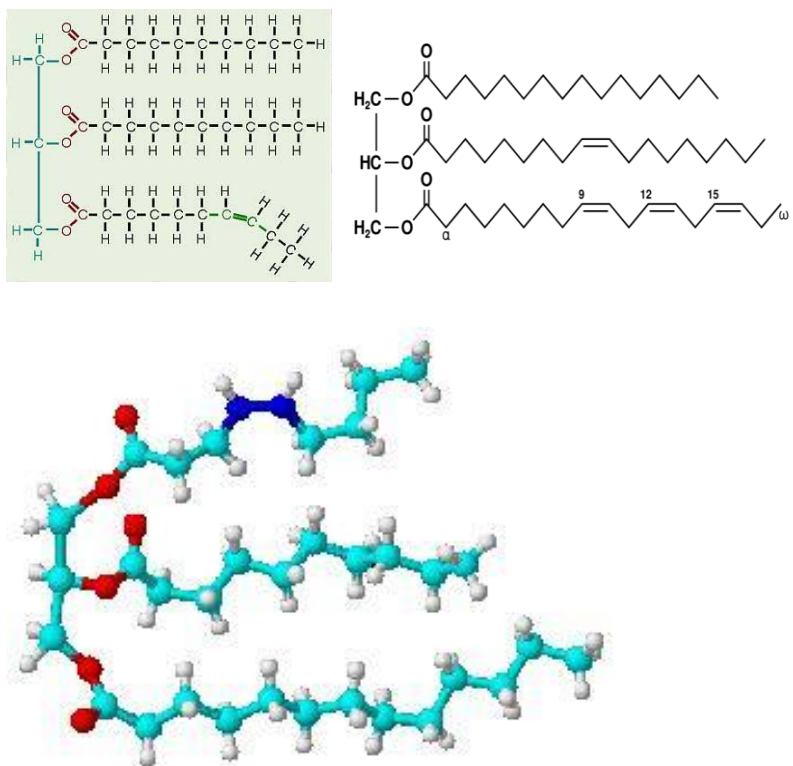


Figure 6 A polyunsaturated model

**Exercise 4:** Construct models of a variety of fatty acids. Make saturated ones such as palmitic (14:0) and stearic (16:0), as well as some unsaturated fatty acids such as oleic (18:1) and linolenic (18:3).

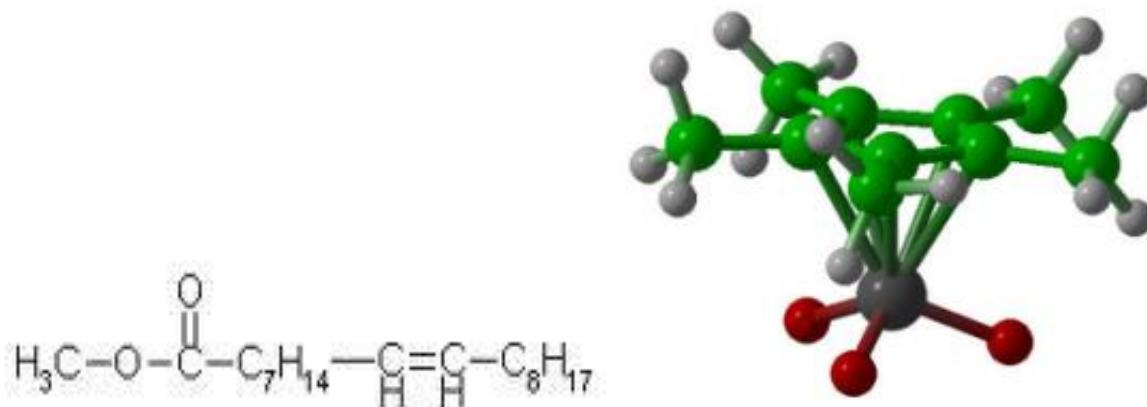
Triglycerides are large and heavy molecules that are made up of three fatty acids connected to a glycerol backbone. They are commonly referred to as fats and oils, and are among a class of molecules called esters. Triglycerides are fatty acid esters of glycerol. The makeup of the fatty acids will vary based on the source. Animal fats tend to be more saturated (no double bonds) while plant oils are typically more unsaturated (having one or more double bonds).



*Figure 7 Molecular structure of triglycerides showing saturated and unsaturated fatty acids*

**Exercise 5:** Using three fatty acids and a glycerol molecule, construct a triglyceride molecule.

Esters are a class of compounds derived from the reaction of an acid and an alcohol. For example, the reaction of fatty acids and methanol produce methyl esters, or biodiesel. The molecular formula for a methyl ester is  $\text{RCO}_2\text{CH}_3$ , where R represents a fatty acid. Triglycerides are also a type of ester. In fact the term “transesterification,” which is the process of turning triglycerides into biodiesel, means the act of changing one type of ester into another.



*Figure 8 Structure of a methyl oleate formula (18:1) and 3-D model of methyl caprylate (10:0).*

**Exercise 6:** Use 3 methanol molecules and 1 triglyceride molecule to construct 3 methyl ester molecules. Each methyl ester molecule may be different, depending on the fatty acid used to make it. You should have one glycerol molecule left over.

### Additional Exercises

- Write the molecular formula for oleic acid (18:1) and draw a diagram of the fatty acid chain.
- On which carbon would you find the double bond in an Omega 3 fatty acid?

## Laboratory 2: Chemical Reactions

### *Topics Covered*

- Periodic Table
- Atomic weights of elements
- Calculating molecular weights using the atomic weights of the elements
- Chemical reactions

### *Equipment Needed (per pair or group)*

- A Periodic Table
- Two 500 mL Erlenmeyer flasks with stoppers
- One 1000 mL Erlenmeyer flask with stopper
- Two beakers
- Glass stirring rods
- Weighing scale (readable to 0.01 g)

### *Reagents Needed (per pair or group)*

- Calcium chloride
- Sodium carbonate

### Background Information -- Molecular Weight

The weight of a molecule is the sum of the weights of the atoms in the molecule. If we know the formula of the molecule, we can calculate the molecular weight.

For example, one of the products used in the manufacturing of biodiesel is ethanol. The formula for ethanol is  $C_2H_6O$ . We can calculate its molecular weight by looking up the individual atom weights. The atomic weight for C (carbon) is 12.011, H (hydrogen) is 1.008, and O (oxygen) is 15.999. From the formula we see that ethanol has 2 carbons, 6 hydrogens, and a single oxygen atom. Adding these up, we get 46.069 for the molecular weight of ethanol as shown in the following table.

ATOM	NUMBER	ATOMIC WEIGHT Of the ATOM	TOTAL WEIGHT
Carbon	2	12.011	24.022
Hydrogen	6	1.008	6.048
Oxygen	1	15.999	<u>15.999</u>
			46.069

## Background Information -- Chemical Reactions

A chemical reaction is when different chemicals come in contact with each other and a change takes place involving the disappearance of a substance and the appearance of a new substance. Accompanying this is a change in the chemical energy of the substances. This change can be either an increase, where heat is absorbed (an endothermic reaction), or a decrease, when heat is released, or transferred to the surroundings (an exothermic reaction).

Another component of chemical reactions is how long it takes: the reaction time. Combustion, for example, is a fast reaction, whereas the reaction between alcohol and vegetable oil in making biodiesel is slower. The following four factors control reaction speed:

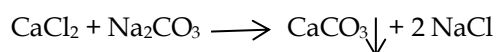
1. The nature of the reacting substance. Reactions between ions generally occur almost instantaneously, for example in a solution, as fast as they can collide with each other.
2. The concentration of the reacting material. Increasing the concentration increases the speed of the reaction. If the reacting material is a gas, increasing the pressure will speed-up the reaction. If dealing with solids, increasing the degree of subdivision, exposing more surface, also increases the reaction speed.
3. The temperature. The higher the temperature, the faster the reaction.
4. The presence of a catalyst.

These four factors are major considerations in making biodiesel, and the industry has developed techniques to speed up the reaction.

Knowing the molecular weight of substances will allow us to combine just the right amount to produce the desired reaction, with nothing left over.

In this laboratory exercise, we are going to dissolve calculated quantities of two substances separately into water, forming ions. When we mix these two solutions, the ions will react very rapidly making a product not soluble in water, and thus dropping out of the action zone. By the use of their molecular weights, we can determine the amount of the two substances we need, with nothing left over to form the non-soluble product.

To show the results clearly and aid in the mixing, we have selected two compounds that will dissolve in water, and when mixed will form a third compound that is not soluble in water and will precipitate out. The compounds are calcium chloride ( $\text{CaCl}_2$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). When mixed together, they will form calcium carbonate ( $\text{CaCO}_3$ ), which is not soluble and will precipitate out.



We see that one calcium chloride molecule combines with one sodium carbonate molecule to form one calcium carbonate molecule. The table salt ( $\text{NaCl}$ ) formed will stay in solution and is of no concern to us in this lab.

Since we do not need to use this much reactant to demonstrate this chemical reaction, divide the molecular weight of calcium chloride and the molecular weight of sodium carbonate by 10.

Therefore, we will weigh out one-tenth gram-molecular weight of each for mixing. If we have mixed the correct amount needed, there will be no calcium chloride or sodium carbonate left in the solution. We can show this by pouring off 2 samples of the solution and adding more calcium chloride to one and more sodium carbonate to the other. If no precipitate appears in either sample, there was no excess. The actual number of atoms and molecules matched the calculated amounts needed to form the calcium carbonate.

## Pre-Lab Exercises

- Calculate the molecular weight of methanol ( $\text{CH}_3\text{OH}$ ), a common alcohol used in biodiesel production.
- Calculate the molecular weight of potassium hydroxide ( $\text{KOH}$ ), a common catalyst used in biodiesel production.

## Laboratory Procedure

1. Take the 2 smaller, 250 mL flasks and fill each with about 200 ml of distilled water.
2. Label one  $\text{CaCl}_2$  and the other  $\text{Na}_2\text{CO}_3$  and put them aside.
3. Using the periodic table, calculate the molecular weights of the two compounds.
4. Weigh out an amount in grams numerically equal to one-tenth the molecular weight of each compound (to the nearest 0.01 g). (For example, if the molecular weight of a particular compound is 50.00, you would weigh out 5.00 grams).
5. Pour the calcium chloride into the flask with the  $\text{CaCl}_2$  label. Insert a rubber stopper and shake until the  $\text{CaCl}_2$  has dissolved.
6. Pour the  $\text{Na}_2\text{CO}_3$  into the flask with the  $\text{Na}_2\text{CO}_3$  label. Insert the stopper and shake until the  $\text{Na}_2\text{CO}_3$  has dissolved.
7. Now pour these two mixtures into the larger flask, insert the stopper, and shake until thoroughly mixed. Observe the precipitate formed, and watch it fall to the bottom.
8. When the upper liquid is clear and free of any precipitate, pour about 50 ml each into two clean beakers. Add a few grams of calcium chloride to one beaker and a few grams of sodium carbonate to the other. Stir until they have dissolved.
9. Was any precipitate formed in the beakers? Why or why not?
10. Was there any cloudiness in one of the beakers? Explain.

## Laboratory 3: Determination of the Acid Number of Vegetable Oils by Titration

### *Topics Covered*

- pH vs. acid number
- Acidity and acid values in organic solutions
- Titration techniques
- How to obtain acid values of vegetable oils

### *Equipment Needed (per pair or group)*

- One graduated titration burette with stand, 50 mL
- Three Erlenmeyer flasks, 250 mL each
- Weighing scale (readable to 0.01g)
- Pipette

### *Reagents Needed (per pair or group)*

- Titrant solution (prepared by instructor)
- Titration solvent (prepared by instructor)
- Phenolphthalein indicator solution (prepared by instructor)
- 2 grams vegetable oil

### Background Information -- Acid number

To make biodiesel, triglycerides (fats and oils) react with an alcohol (such as methanol) to produce methyl fatty acid esters and glycerol. A catalyst such as potassium hydroxide or sodium hydroxide is added to speed up the process. However, if the oil or fat is degraded and has a lot of free fatty acids (fatty acids not attached to a glycerol backbone), these free fatty acids can react with the catalyst first to create soap, which must be removed. Therefore, before making biodiesel it is necessary to determine the amount of free fatty acids in the oil or fat, in order to know how much catalyst to add.

Fats and oils with high free fatty acid levels include waste vegetable oil and animal fats. These feedstocks are cheaper to use than food-grade vegetable oil, and so are often desirable as feedstocks for making biodiesel.

You are probably familiar with the concept of “pH” to measure the acidity or alkalinity of an aqueous solution (a solution of a substance dissolved in water). pH can be measured using pH paper or a pH meter. The pH number indicates the strength of the acid. The stronger the acid, the lower the pH number.

Can we use pH paper or a pH meter to figure out how much free fatty acids are in a sample of oil or fat? Unfortunately, we cannot, because pH will not tell us *how much* acid we have—it will only tell us the strength of the acid.

When making biodiesel, we need to know not the strength of the acid, but the *amount* of free fatty acids (FFAs) present.

In addition, pH is not applicable in a fat or oil, because the hydrogen in organic solutions does not dissociate into hydrogen ions. Acidity exists in organic solutions containing acidic functional groups such as carboxyl groups ( $-\text{COOH}$ ), which are found in fatty acids<sup>[1]</sup>.

Instead of pH, we have to use a measure called the acid number. The acid number is a measure of the acidity in a non-aqueous solution (non-water solution) such as an organic solution.

The acid number is expressed as the quantity of a known concentration of potassium hydroxide (KOH) consumed by titrating one gram of a sample in the units of milligrams (mg) of KOH per gram of sample, i.e.,  $\text{mg KOH/g}$  of sample.

Since organic solutions are not usually miscible with aqueous potassium hydroxide solutions, the addition of another solvent that helps the organic chemical dissolve in an aqueous solution is typically needed.

With manual titration, a color indicator, such as phenolphthalein, is needed.

## Background Information -- Acid-Base Titration

Titration is a wet-chemistry practice to determine the concentration of an unknown chemical in a solution. An acid-base titration is a titration that uses a known concentration of an acid (or base) solution, such as hydrochloric acid (or potassium hydroxide), to react with an unknown base (or acid) in solution.

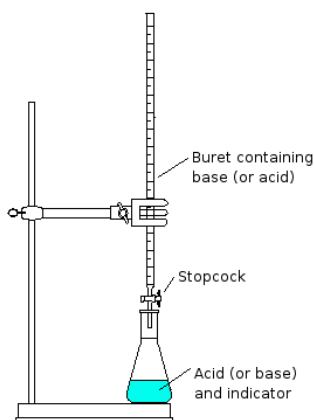


Figure 1 Illustration of a titration set-up

After the base (or acid) is all consumed, the solution is neutral. Any small amount of acid (or base) added after this point will cause the solution to rapidly become acidic (or basic).

Based on the acid (or base) consumed, the concentration of the unknown base (or acid) can be calculated. The originally known concentration solution is then called the standard solution of titrant, which is used to titrate the unknown.

Most titrations are conducted in aqueous solutions, such as acid-base titration. If the sample to be titrated is water insoluble (such as oil), a co-solvent or a different solvent other than water is needed.

<sup>1</sup> Sometimes, the acidity of an organic solution can be also contributed by Lewis acids, which do not contain carboxyl groups but behave like an acid due to the fact that they are electron receivers or proton donors. A Lewis acid is any specie that accepts electrons.

The equipment for performing titrations manually can be simply a calibrated burette for the standard titrant solution, and a volumetric flask that contains a precise volume of the unknown solution. An indicator, such as phenolphthalein, is needed to provide visual indication for the endpoint.

Automated titration devices are also available to perform titrations with high efficiency and accuracy, and are widely used in commercial applications.



Fig. 2: Auto-titrator

## Pre-Lab Questions

- How is pH different from acid value?
- Why is pH not used when measuring the amount of acid in an oil or fat?

**Instructor Note:** Please see page 3 for preparing the titrant and the titration solvent.

**Safety Note:** In this lab you will be using solutions containing isopropyl alcohol and toluene, which are both highly flammable. Keep these away from heat or flames. The titrant contains potassium hydroxide, which is caustic and can burn skin and harm eyes. Wear gloves, a lab coat or apron, and eye protection when using potassium hydroxide.

## Laboratory Procedure

1. Weigh flask and record the weight on Table 1.
2. Weigh approximately 1 g of oil sample to the nearest 0.01 g <sup>[2]</sup> and transfer to the titration flask.
3. Record the sample size in Table 1.
4. Add 125 mL of titration solvent into the flask containing the sample.
5. Add a couple of drops of the phenolphthalein indicator into the solution.
6. Swirl the solution vigorously for approximately 1 minute to ensure the uniformity of the solution.
7. Prepare a second sample for titration by repeating the steps a) through f)
8. Prepare a blank/ reference with only titration solvent and phenolphthalein indicator (no oil) by repeating steps a) through f).
9. Fill the burette with the titrant solution.
10. Record the starting volume of titrant on Table 1.
11. Carefully introduce the titrant from the burette into the flask while swirling the solution vigorously but without spattering.
12. Stop introducing titrant if the solution changes color to pink.
13. Record the ending volume of titrant on Table 1.
14. Repeat the steps i) through m) for the second sample.

<sup>2</sup> This is based on an expected acid number of between 5 and 20; if acid number is higher than 20, a sample size of 0.25 g is recommended; if the acid number is lower than 5, a sample size of 5.0 g is recommended.

15. Repeat the steps i) through m) for the blank (please note that the blank requires a much smaller volume of titrant because of its low acidity).

Table 1 Raw data recoding

Category	Variable	Quantity	Sample #1	Sample #2	Blank #b
Sample size	$W_{ini}$	Flask weight (g)			--
	$W_{end}$	Flask + sample (g)			--
	$W$	Net sample size (g)			--
Titration volume	$V_{ini}$	Starting vol. (mL)			
	$V_{end}$	Ending vol. (mL)			
	$V$	Net volume (mL)			

### Data Processing

Acid number calculation:

$$A_1 = 56.1 \cdot \frac{(V_1 - V_b) \times C}{W_1} \quad A_2 = 56.1 \cdot \frac{(V_2 - V_b) \times C}{W_2} \quad \text{and}$$

$$A = \frac{A_1 + A_2}{2}$$

Where:  $A_1$ ,  $A_2$ , and  $A$  are the acid numbers of sample #1, sample #2, and average, respectively (mg KOH/g)

$V_1$ ,  $V_2$  and  $V_b$  are the net titrant volumes for titrating sample #1, sample #2, and blank, respectively (mL)

$W_1$  and  $W_2$  are the net sample sizes of sample #1 and sample #2 (mL)

$C$  is the concentration of the standard solution (M or mol/L) provided by the instructor

Relative precision of the titration: <sup>[3]</sup>

$$p\% = \left| 1 - \frac{A_1}{A_2} \right| \times 100\%$$

Where:  $p\%$  the relative precision of the titration (in %)

<sup>3</sup> If the relative precision is less than a certain value, e.g., 2%, conducting another sample titration is typically recommended.



$A_1$  and  $A_2$  are the acid numbers of sample #1 and sample #2 ( $mg$   $KOH/g$ )

## Laboratory 4: Chemical Equilibrium in Biodiesel Production

### *Topics Covered*

- Forward chemical reactions vs. reverse reactions
- Chemical reactions in equilibrium
- Ways to stimulate a reaction to proceed towards completion
- Chemical reactions involved in biodiesel production

### *Equipment Needed (per pair or group)*

- 250 mL flask and small watch glass or stopper
- 125 mL Erlenmeyer flask and stopper
- Separatory funnel, 250 mL
- Stirring hot plate and magnetic stir bar
- Thermometer
- Aluminum foil
- Weighing scale (accurate to 0.001g)

### *Reagents Needed (per pair or group)*

- 20 grams methanol (anhydrous, reagent grade)
- 1 gram potassium hydroxide (as catalyst)
- 100 grams soybean oil (representative molecular weight = 877 g/mol) (can be replaced by canola oil, or other types of virgin vegetable oil)

### Background: Introduction to Chemical Equilibrium

Chemical reactions can go forwards and backwards at the same time. Substances in a closed container can react with each other to produce new substances (referred to as the “forward reaction”); these new substances can also react with each other to form the original substances (referred to as the “reverse reaction”).

As a chemical change starts, the quantities of the components on the left side of the reaction equation will decrease, and those on the right side will increase. The eventual results depend on the nature of the overall reaction. A reversible reaction is a reaction in which both the forward and reverse reactions are significant. An example is sodium chloride (NaCl) reacting with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) to produce sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and hydrochloric acid (HCl):



Notice that two molecules of NaCl react with one molecule of H<sub>2</sub>SO<sub>4</sub> to produce one molecule of Na<sub>2</sub>SO<sub>4</sub> and two molecules of HCl. Once sufficient amounts have been produced, Na<sub>2</sub>SO<sub>4</sub> will react with HCl to produce NaCl and H<sub>2</sub>SO<sub>4</sub>. Reversible reactions are commonly written with double arrows pointing in opposite directions, showing that the reaction can proceed in either direction.

Strictly speaking, all chemical reactions are reversible reactions. However, some reactions result in a final product mixture such that the reverse reaction is so insignificant, and the reactant concentrations are at such negligible quantities after reaction, that these reactions are considered irreversible. An example of an irreversible reaction is the reaction between calcium chloride (CaCl<sub>2</sub>) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), which produces calcium carbonate (CaCO<sub>3</sub>) and sodium chloride (NaCl):



In this reaction, the product CaCO<sub>3</sub> is a solid that precipitates out to the bottom of the liquid solution container. Its concentration in the solution is so low that it hardly ever reacts with NaCl in solution to form CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> again. Therefore, it is generally considered an irreversible reaction. Notice that the equation for this irreversible reaction is indicated by a one-direction arrow.

Given sufficient time, an overall reaction will appear stopped, i.e., the concentrations of reactants and products in the system remain unchanged, although the forward reaction and the reverse reaction may still be going on. The reaction appears stopped because the forward reaction proceeds at the same rate as the reverse reaction. The reaction system at this state is in chemical equilibrium (or in dynamic equilibrium).

Therefore, reversible reactions can be explained from the point of view of chemical equilibrium. A chemical reaction is said to be incomplete, or reversible, when the reaction is in an equilibrium state in which significant quantities of both reactants and products are present. It is said to be complete, or irreversible, when the reaction is in an equilibrium state in which only significant quantities of products are present.

Chemical equilibrium is important in order to predict the reactant conversion rate or the product yield from a chemical reaction. To explain this, a generic chemical reaction occurring in solution (or reaction in liquid phase) with arrows pointing both ways indicates that the overall reaction is reversible, as shown below:



Where: *A*, *B*, *P*, and *S* are chemical species involved in the reaction, and *a*, *b*, *p*, and *s* are the stoichiometric coefficients of the corresponding species in the reaction.

The law of mass action explains and predicts the behaviors of chemical reaction solutions in a mathematical form. It describes the rates of forward and reverse reactions in the system, and defines the equilibrium of the overall chemical reaction and the composition of chemical species in the system. The law of mass action states that any chemical change is a competition between a forward reaction and a reverse reaction.

For eq. (1), the rates of reaction ( $r_A$  and  $r_p$ ) can be written as:

$$\text{Rate of forward reaction on reactants: } r_A = k_A \cdot [A]^a \cdot [B]^b \quad \text{eq. (4)}$$

$$\text{Rate of reverse reaction on products: } r_p = k_p \cdot [P]^p \cdot [S]^s \quad \text{eq. (5)}$$

Where:  $[A]$ ,  $[B]$ ,  $[P]$ , and  $[S]$  are the concentrations of chemical species in the reaction;  $k_A$  and  $k_p$  are the corresponding rate constants.

It is said that a chemical reaction is in equilibrium if the rate of the forward reaction is the same as that of the reverse reaction. When the rate of forward reaction is the same as the rate of reverse reaction (i.e.,  $r_A = r_p$ ), it is said that the overall reaction reaches a dynamic equilibrium, i.e., the overall reaction appears to have stopped but is continuing in both directions at the same rate (Fig. 1).

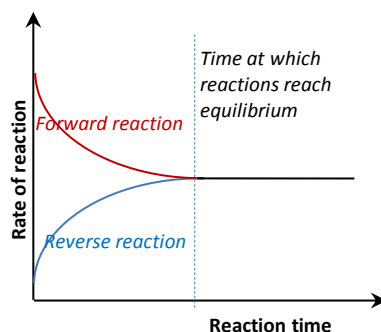


Figure 1. Illustration of forward and reverse reaction at equilibrium.

At the equilibrium point, the concentrations of  $[A]$ ,  $[B]$ ,  $[P]$ , and  $[S]$  remain constant, and an Equilibrium Constant  $K_{eq}$  is used to describe the relationship among the concentrations at a given temperature:

$$K_{eq} = \frac{k_A}{k_p} = \frac{[P]^p \cdot [S]^s}{[A]^a \cdot [B]^b} \quad \text{eq. (6)}$$

$K_{eq}$  is temperature dependent, and may carry units based on the stoichiometric coefficients of the reaction. For example, in the following reaction,



The value of  $K_{eq}$  at 300 K is  $4 \times 10^{31}$  and dimensionless. This value of  $K_{eq}$  will decrease to  $4 \times 10^{18}$  if the temperature is increased to 500 K,<sup>4</sup> which indicates that increasing the temperature of the system favors the reverse reaction or the decomposition of the gaseous product HCl.

When a chemical reaction is at equilibrium, any change of the system process parameters will alter the composition to a new equilibrium state following Le Chatelier's principle. Le Chatelier's principle states that if a change in temperature, pressure, or concentration of chemical species is introduced in a chemical reaction in equilibrium, the reaction system will shift its equilibrium composition in a way that tends to counteract this change of variable. According to Le Chatelier's principle, a reaction system can be affected and then reach a new equilibrium in several ways, such as:

- 1) adding or removing reactants or products from a reaction system
- 2) increasing or decreasing partial pressures of reactants and/or products in a gaseous reaction system, and
- 3) increasing or decreasing the temperature of the reaction system

Generally speaking,

- 1) Adding a chemical species that is neither a reactant nor a product will not affect the chemical equilibrium (if the reaction system is a liquid phase reaction, or the added chemical does not affect the total pressure of the system). For example, a heterogeneous catalyst does not belong to a reaction system. Therefore, adding a catalyst to a system will affect both the forward reaction and the reverse reaction in the same way and reduce the time at which equilibrium is reached, but will not affect the equilibrium constant (i.e., the equilibrium constant remains the same numeric value).
- 2) Changing the partial pressure of a gaseous reactant (or a gaseous product) in a gas-phase reaction system of fixed reaction volume is equivalent to changing the concentration of the gaseous reactant (or the gaseous product), and thus will change the chemical equilibrium.
- 3) Changing the temperature of the reaction system may shift the chemical equilibrium because the temperature may affect the rates of forward and reverse reactions (i.e.,  $k_A$  and  $k_P$ ) differently. Note that the temperature affects the rate of reaction based on the Arrhenius' Law:  $k_i = k_0 e^{-E/RT}$ . Where  $k_i$  is the rate of reaction at a given temperature in  $\text{kmol}/\text{m}^3 \text{ s}$ ,  $k_0$  the temperature-independent coefficient in  $\text{kmol}/\text{m}^3 \text{ s}$ ,  $E$  the activation energy in  $\text{kJ}/\text{kmol}$ ,  $R$  the universal gas constant of  $8.314 \text{ kJ}/\text{kmol} \cdot \text{K}$ , and  $T$  the given temperature in K.

<sup>4</sup> Chemical Equilibrium at <http://pages.towson.edu/ladon/chemeq.html>. Accessed on July 2, 2012.

Transesterification is a reversible reaction and will reach equilibrium as the reaction proceeds (Figure 2). Each triglyceride contains three chains of fatty acids connected by a glycerol backbone. To replace the glycerol from these three fatty acids, three moles of methanol are needed, each reacting with one fatty acid.

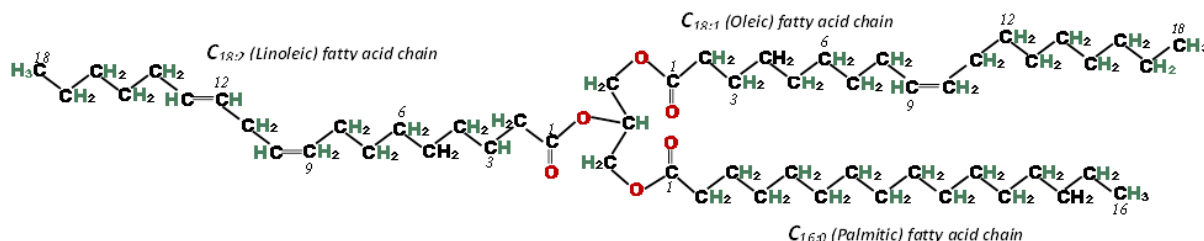
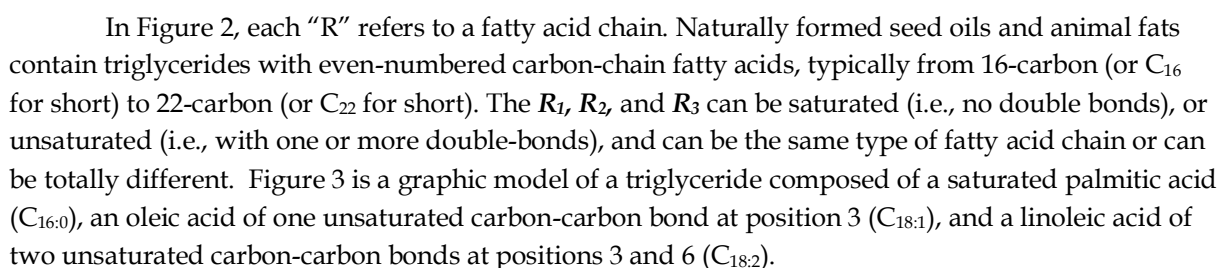


Figure 3. An example of triglyceride structure

The transesterification reaction actually happens in three steps. Each is a reversible reaction with methanol:

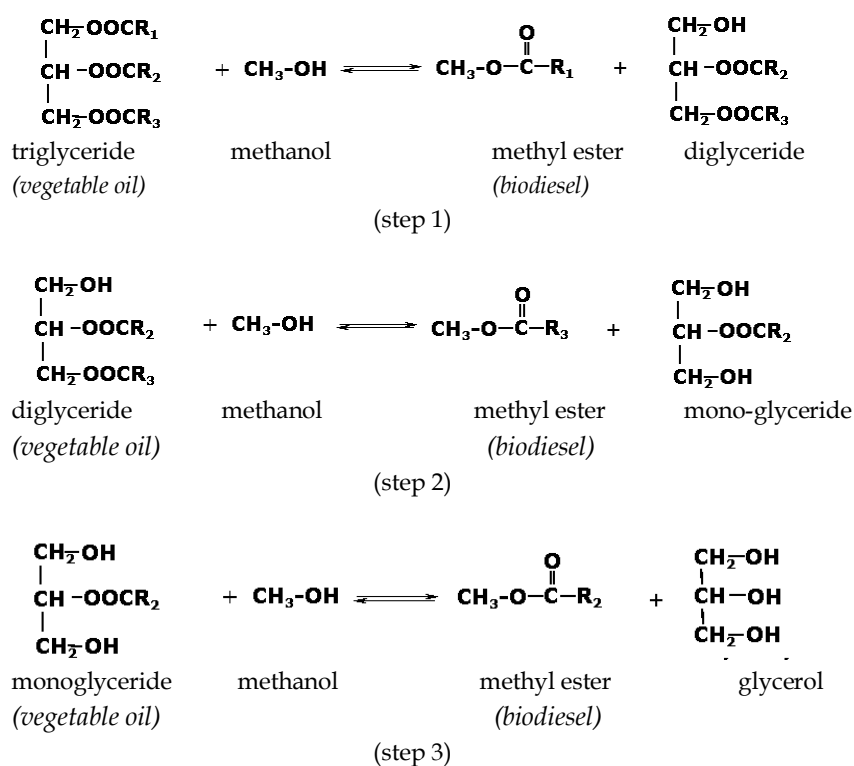


Figure 4. Transesterification of triglycerides with methanol stepwise.

These three reactions do not occur at the same reaction rate, and Step 2 (i.e., the reaction of diglyceride to mono-glycerides) is the limiting step, as illustrated in Figure 5.

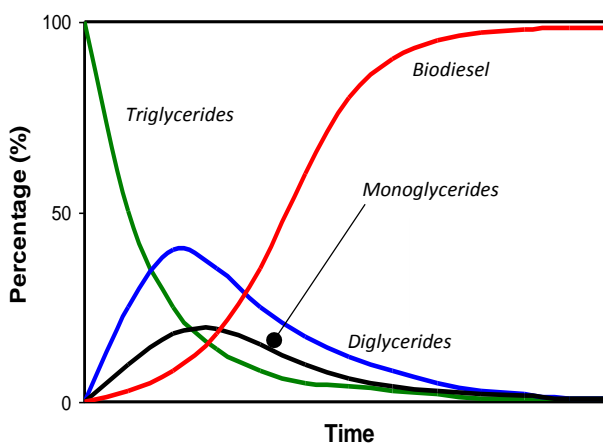


Figure 5. Illustration of conversion rates in transesterification of triglycerides with methanol.

Since transesterification is a reversible reaction, if stoichiometric reactants are used, i.e., 3 mol of methanol reacting with 1 mol of triglyceride, the reaction will reach equilibrium after a certain reaction time. At that time the reaction mixture will contain esters, mono-glycerides, and di-glycerides, as well as the reactants of triglycerides and methanol. Since biodiesel producers are interested in producing as much biodiesel as possible by converting all of the oil or fat in the system, they generally add twice as much methanol as stoichiometrically required (i.e., 100% excess, or a methanol to oil molar ratio of 6:1). The additional methanol drives the reaction towards the biodiesel, resulting in a completion of triglyceride conversion to biodiesel, according to Le Chatelier's principle.

In this laboratory, we will be learning the concept of chemical equilibrium by experimenting with converting soybean oil, a vegetable oil composed of triglycerides, into biodiesel through a two-step process.

### Pre-Lab Questions:

1. Why do some reactions reverse themselves, while others do not?
2. What are some things you can do to force a reaction in one direction?
3. What do biodiesel producers do to push the transesterification reaction in the direction of biodiesel production?

**Safety Note:** Because of the potentially dangerous chemicals used in this lab, everyone must wear safety glasses or goggles while working in the laboratory. Lab coats or aprons should be worn when

pouring or mixing chemicals. If a fire occurs, leave the building immediately and call 911 . Do not try to fight it!

## Laboratory Procedure

Procedure for making a small batch of biodiesel in two stages

### *Stage 1 Transesterification with stoichiometric reactants*

1. Weigh out 1 g of potassium hydroxide into a 125 mL Erlenmeyer flask. Into this same flask add 20 g of methanol to an accuracy of 0.01 g (this amount is equivalent to 6:1, or twice the stoichiometric molar ratio of methanol to oil). Add a stir bar, cover with aluminum foil, and place on a magnetic stirrer. Mix until the KOH is completely dissolved. Set this aside.
2. Weigh an empty 250 mL Erlenmeyer flask and record the weight (to an accuracy of 0.01 g) in Table 1 (this will be used later to calculate your biodiesel yield). Weigh out about 100 g of soybean oil to an accuracy of 0.01 g into this same flask and record in Table 1. Add a stir bar, put on a hot plate, and start to heat the oil to around 60 °C.
3. Once 60 °C is reached, add half (or approximately 10 g) of the alcohol/catalyst mixture to the flask (this will give you close to a 3:1 or stoichiometric molar ratio of methanol to oil) and cover with a watch glass or aluminum foil to keep the alcohol vapors from escaping. Stir this mixture at a moderate level at 60 °C to react for 60 min.
4. Stop heating and stirring. Carefully transfer the mixture to a separatory funnel and allow it to cool down and separate for 20 min. <sup>5</sup>
5. Weigh a 125-mL flask (to an accuracy of 0.01 g) and record the weight. Remove the glycerol (lower) layer carefully from the bottom of the funnel into this pre-weighed flask. The upper layer is the biodiesel phase, and the separated lower layer is the crude glycerol with some catalyst in it.
6. Weigh the flask with separated glycerol (to an accuracy of 0.01 g) and record the net weight into Table 1.
7. Save the biodiesel phase for later use.

The first step of the reaction is now finished. Based on the crude glycerol weight, calculate the estimated biodiesel yield, and compare this with the theoretical yield, assuming 100% soybean oil conversion<sup>6</sup>. Discuss:

<sup>5</sup> **Note:** If there is no phase separation after 5 to 10 min, it can be forced by adding water to it. Return the mixture to the 250 mL Erlenmeyer flask, while stirring, add 15 mL of water and continue to stir for about 10 seconds. Then, return the mixture to the separatory funnel. This action will concentrate the polar molecules of water, methanol and glycerol and allow them to settle along with a good portion of the soap (the undesired byproduct).

<sup>6</sup> **Hint:** the theoretical molar yield of biodiesel is the same as the theoretical yield of glycerol based on the stoichiometric ratios in the transesterification (Fig. 2 ). For every mol of soybean oil (MW = 877 g/mol), there is 1 mol of glycerol formed (glycerol MW = 92.1

- How much soybean oil has converted to biodiesel? Has all the soybean oil been converted? Is the reaction complete?
- If not, could the reaction be complete if we extended the reaction time by another 2 hours? Why or why not?
- According to Le Chatelier's principle and the nature of transesterification, what is/are the possible way(s) you could improve the conversion of soybean oil (or to help the reaction move forwards to the right)?

## *Stage 2 Transesterification with additional methanol (to complete the reaction)*

1. Transfer the saved biodiesel from the previous step into the original reaction flask. Add a stir bar, put on a hot plate, and start to heat the solution again to around 60 °C.
2. Once 60 °C is reached, add the remaining alcohol/catalyst mixture to the flask and cover with a watch glass or aluminum foil to keep the alcohol vapors from escaping. Stir this mixture at a moderate level for 60 min at 60 °C to react.
3. Stop heating and stirring. Carefully transfer the mixture to a separatory funnel and allow it to cool down and separate for 20 min.<sup>7</sup>
4. Remove the glycerol (lower) layer carefully from the bottom of the funnel into the same flask containing crude glycerol from the previous stage.
5. Weigh the flask with the separated glycerol and record the net weight (to an accuracy of 0.01 g) into Table 2.

Based on the crude glycerol weight, again calculate the estimated biodiesel yield, and compare this with the theoretical yield, assuming 100% soybean oil conversion<sup>8</sup>. Discuss:

- How much soybean oil has converted to biodiesel? Has all the soybean oil been converted? Is the reaction complete?

g/mol). For 100 g soybean oil used for this laboratory, it is equivalent to  $100 \text{ g} / 877 \text{ g/mol} = 0.114 \text{ mol}$ ; the theoretical yield of glycerol will be  $0.114 \text{ mol}$  or  $0.114 \times 92.1 \text{ g/mol} = 10.5 \text{ g}$ .

<sup>7</sup> **Note:** If there is no phase separation after 5 to 10 min, it can be forced by adding water to it. Return the mixture to the 250 mL Erlenmeyer flask, while stirring, add 15 mL of water and continue to stir for about 10 seconds. Then, return the mixture to the separatory funnel. This action will concentrate the polar molecules of water, methanol and glycerol and allow them to settle along with a good portion of the soap (the undesired byproduct).

<sup>8</sup> **Hint:** the theoretical molar yield of biodiesel is the same as the theoretical yield of glycerol based on the stoichiometric ratios in the transesterification (Fig. 2 ). For every mol of soybean oil (MW = 877 g/mol), there is 1 mol of glycerol formed (glycerol MW = 92.1 g/mol). For 100 g soybean oil used for this laboratory, it is equivalent to  $100 \text{ g} / 877 \text{ g/mol} = 0.114 \text{ mol}$ ; the theoretical yield of glycerol will be  $0.114 \text{ mol}$  or  $0.114 \times 92.1 \text{ g/mol} = 10.5 \text{ g}$ .

# Biodiesel Fundamentals for High School Chemistry Classes



## *Laboratory Observations*

Color change of the reaction mixture from start to finish point:

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Glycerol formation and separation:

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## Data collection and processing

Table 1

Category	Item	Variable	Quantity (g)
Soybean oil	Flask weight	$W_{ini}$	
	Flask + sample	$W_{end}$	
	Net sample size	$W_{soy}$	
Crude glycerol	Flask weight	$W_{ini,1}$	
	Flask + sample	$W_{end,1}$	
	Net sample size	$W_{gly,1}$	

Calculate the soybean oil (MW = 877 g/mol) added in moles:

$$m_{soy} = W_{soy} / 877 \text{ (mol)}$$

This is the equivalent molar amount of theoretical glycerol yield, or

$$m_{soy} = m_{gly,theo}$$

Actual glycerol (MW = 92.1 g/mol) molar yield in this stage:

$$m_{gly,actual,1} = W_{gly,1} / 92.1 \text{ (mol)}$$

Therefore, the degree of overall reaction (or overall conversion of soybean oil) is:

$$R_1(\%) = m_{gly,actual,1} / m_{gly,theo} \times 100$$

Table 2

Category	Item	Variable	Quantity (g)
Crude glycerol	Flask + previous sample	$W_{ini,2}$	
	Flask + new sample	$W_{end,2}$	
	Net total sample size	$W_{gly,2}$	

Actual glycerol (MW = 92.1 g/mol) molar yield in this stage:

$$m_{gly,actual,2} = W_{gly,2} / 92.1 \text{ (mol)}$$

Therefore, the degree of overall reaction (or overall conversion of soybean oil) is:

$$R_2(\%) = m_{gly,actual,2} / m_{gly,theo} \times 100$$

## Laboratory 5: Transesterification of Vegetable Oil and Alcohol to Produce Ethyl Esters (Biodiesel)

### *Topics Covered*

- Transesterification of vegetable oils or animal fats as a reversible chemical reaction
- The role of catalyst in transesterification of vegetable oils or animal fats
- The use of ethanol (rather than the more common methanol) in biodiesel production
- The importance of temperature and agitation/mixing for the chemical reaction
- Side reactions competing with transesterification
- Separation of co-product glycerol

### *Equipment Needed (per pair or group)*

- 250 mL flask or beaker, and small watch glass or stopper
- 125 mL Erlenmeyer flask and stopper
- Separatory funnel, 250 mL
- Stirring hot plate and 2 magnetic stir bars
- Thermometer
- Aluminum foil
- Weighing scale (readable to 0.01 g)

### *Reagents Needed (per pair or group)*

- Ethanol (anhydrous, 100%)
- 1 gram potassium hydroxide
- 100 grams vegetable oil, tallow, or lard (food grade)

### Background Information -- Transesterification

According to the current American Standards for Testing Materials (ASTM), biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, for use in compression-ignition (diesel) engines.

One process for making biodiesel is called transesterification. This is a chemical reaction in which 1 mole of triglycerides (vegetable oil or animal fats) reacts with 3 moles of alcohol to produce 3 moles of alkyl esters (biodiesel) and 1 mole of glycerol, a co-product. This is a reversible, equilibrium reaction and requires excess alcohol to push it toward the products side. Usually, 6 moles of alcohol are used per 1 mole of triglycerides. Le Chatelier's principle explains this behavior. This principle, named after Henry Le Chatelier, can be summarized as follows:

If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established.

Typically, a strong base such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) is used as the catalyst, which normally would not be consumed during this reaction and would end up in the glycerol layer. This is not always the case, as we will see later.

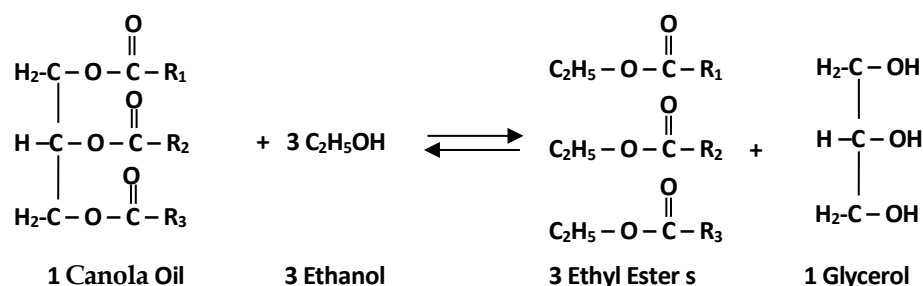
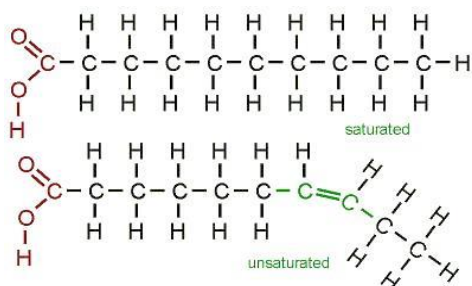
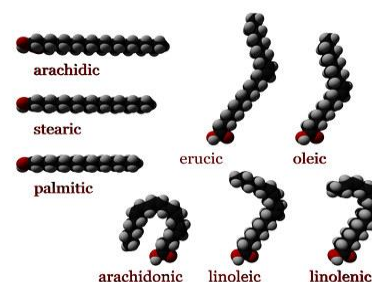


Figure 1 - The Transesterification Reaction

A triglyceride is a molecule made up of three fatty acids attached to a glycerol backbone. Figure 1 shows a depiction of the reaction where the R's represent the fatty acids that make up a triglyceride. The three fatty acids on each molecule could be the same or they could be different. Each oil or fat has a unique fatty acid profile. Canola, for example, is high in oleic acid which is an 18 carbon chain with one double bond. It also contains linoleic acid as well as a number of other less prominent fatty acids.



The fatty acid makeup of the oil or fat is responsible for some of the properties found in the resulting biodiesel. The more *saturated* (no double bonds) the oil or fat is, the more stable the biodiesel (the less likely it is to go rancid). However, the cold flow properties tend to be poorer as the saturation increases. In other words, saturated fats tend to solidify at higher temperatures than do unsaturated oils.

These trends are reversed as the level of unsaturation (number of double bonds) increases. Notice, in the pictures to the left, that unsaturated fatty acids are bent, and therefore do not readily stack up to form a crystalline structure. These crystals are often associated with filter plugging during cold weather. On the other hand, the saturated fatty acids are

straight and will stick together to form crystals at higher temperatures, causing biodiesel made from saturated fats to gel (and clog up the engine) even at temperatures significantly above freezing.

You can see in Figure 1 that it takes three molecules of ethanol for each molecule of triglyceride to satisfy a complete reaction. This would be a 3:1 molar ratio of alcohol to oil. Typically in practice, a 6:1 molar ratio is used to drive the reaction to the product side. What happens to the excess alcohol that was not used in the reaction? It is unused at the end of the process and separates partly with the fuel and partly with the glycerol. It can be recovered and reused through a process of distillation.

The transesterification reaction will proceed quickly at first and eventually slow down as it reaches equilibrium. At this point, there will be some unreacted glycerides left in the biodiesel. It is possible to improve the quality by removing the glycerin that has settled out and to run another reaction, thus pushing the equilibrium point further to the products side. For this lab, one reaction should be enough to get a good separation of the glycerin from the biodiesel.

To calculate the mass of alcohol needed to achieve a 6:1 molar ratio, you will need the molecular weights of the triglycerides and the alcohol being used. In this example, canola oil and ethanol are the reactants.

It can be very difficult to calculate the molecular weight of a fat or oil, since they are made up of many different large molecules (triglycerides), each with different fatty acids attached. For this exercise we will use a value of 877 g/mol for canola.

Ethanol is not completely soluble in fats and oils, so vigorous mixing is required. As the reaction proceeds the product (alcohol esters) acts as a co-solvent, making the two reactants miscible improving contact and interaction.

For most chemical reactions, temperature plays a major role. There is a rule of thumb that states “for every 10 °C rise in temperature the speed of the reaction doubles.” To increase the reaction rate, it’s relatively easy to increase the temperature. For an unpressurized reactor the temperature should not exceed the boiling point of the alcohol (78 °C for ethanol) for the obvious reason that the ethanol will boil away and the reaction will stop and in some cases reverse. A pressurized reactor, although requiring specialized construction, would allow for a higher temperature reaction and thus a faster reaction rate.

Sometimes an unfortunate side reaction called saponification occurs. This is the process of making soap. Whenever triglycerides (oils and fats), a strong base (sodium or potassium hydroxide), and water come together, soap is formed. Oils and fats used for cooking tend to oxidize due to high temperatures and contact with water. This can cause some of the fatty acids to break off the glycerol backbone and float free. These are referred to as *free fatty acids* (FFA) as shown in Figure 2. They will quickly react with the catalyst to form soaps, destroying some of the catalyst in the process. This reaction proceeds much faster than transesterification. In this case, extra catalyst will be needed to



*Biodiesel can be made from a variety of feedstocks.*

carry out the transesterification reaction. In the case of oils with very high FFA, an acid or enzyme catalyst has to be used to cause the *esterification* of the FFAs to biodiesel.

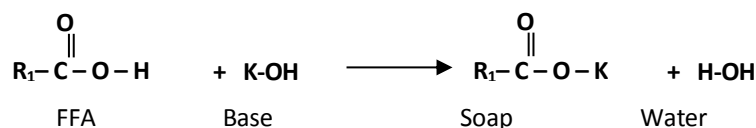


Figure 2 - The Saponification Reaction

Why is this unfortunate? Soap is a long molecule that has a polar head and a non-polar tail. While polar substances are not usually soluble in non-polar solvents, and vice-versa (like dissolves like), soap has properties of both, making it a perfect substance to clean non-polar oil and grease off your hands using water. However, soap can complicate the separation of the non-polar esters from the polar glycerol, water and alcohol.

Normally, glycerol, water and alcohol are not very soluble in biodiesel. They tend to hang on to each other and separate quickly by gravity from the biodiesel due to their higher combined density. However, the more soap that is present, the more these compounds become soluble in each other. This makes it harder for them to separate, which causes a loss of yield (less biodiesel produced). If a small amount of water is added at the end of the reaction it can shift the phase equilibrium in favor of a more complete separation.

## Pre-Lab Exercises

1. Log on to the triglyceride molecular weight calculator:  
<http://www.cals.uidaho.edu/bioenergy/molecularCalculator.asp>
2. Check the molecular weights of the fats and oils in the pull-down menu.
3. Compare the molecular weight of rapeseed oil to that of palm kernel oil. What differences do you see in the fatty acid make-up of these two? Why do think there is a big difference in molecular weights of these two triglycerides?

**Safety Note:** Because of the potentially dangerous chemicals used in this lab, everyone must wear safety glasses or goggles while working in the laboratory. Lab coats or aprons should be worn when pouring or mixing chemicals. If a fire occurs, leave the building immediately. Do not try to fight it!

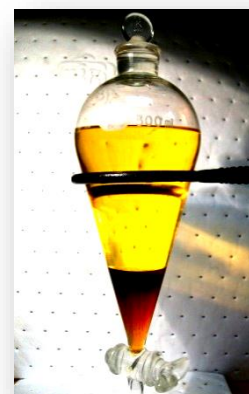
## Laboratory Procedure

The following procedure will be used to make a small batch of biodiesel

1. Calculate the molecular weight of ethanol.
2. Since we are using 100 g of oil, we can use the following relationship to calculate the ethanol needed for a 6:1 ratio of methanol moles to triglyceride moles:

$$\frac{100 \text{ g of oil}}{877 \text{ g/mol}} = \frac{X \text{ g of ethanol}}{6 * (46 \text{ g/mol})}$$

3. Following safe lab procedures, weigh out 1 g of potassium hydroxide into a 125 mL Erlenmeyer flask. Into this same flask add the calculated amount ethanol (from step b).
4. Add a magnetic stir bar, cover with aluminum foil or a watch glass, and place on a stirring hot plate. Mix until the KOH is completely dissolved. Set this aside and go to the next step.
5. Weigh an empty 250 mL Erlenmeyer flask and record the weight in table 1. Into this same flask weigh out about 100 g of the oil or fat to be converted to biodiesel. Again record the exact weight in table 1. Add a stir bar, put on a hot plate, and heat to around 60 °C.
6. Next, add the alcohol/catalyst mixture to the oil in the flask and cover with a watch glass or aluminum foil to keep the alcohol vapors from escaping. Stir this mixture at a moderate level for 60 minutes while holding the temperature at 60 °C.
7. Transfer the mixture to a separatory funnel and allow it to settle for 20 minutes.
8. Remove the glycerin (lower) layer; the upper phase is the biodiesel.
9. **Note:** If there is no phase separation after 5 to 10 minutes, it can be forced by the addition of water. Return the mixture to the 250 mL Erlenmeyer flask, and while stirring, add 15 mL of water and continue to stir for about 10 seconds. Then, return the mixture to the separatory funnel. This action will concentrate the polar molecules of water, ethanol and glycerol and allow them to settle along with a good portion of the soap.
10. Weigh a clean 250 mL beaker or 250 mL Erlenmeyer flask and record the weight in table 1. Next weigh the clean biodiesel and record that weight to be used for the yield calculation.



## Observations

How quickly did the glycerol layer form in the bottom of the separatory funnel?

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Did you have to add water to effect the separation?

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What qualities does the biodiesel have compared to the starting material? (color, smell, viscosity)

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What qualities does the crude glycerol have?

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## *Data collection*

**Table 1**

Category	Item	Variable	Quantity (g)
Oil	Flask weight	$W_{ini}$	
	Flask + sample	$W_{end}$	
	Net sample size	$W_1$	
Biodiesel	Flask weight	$W_{ini}$	
	Flask + sample	$W_{end}$	
	Net sample size	$W_2$	

### Data processing

- a. Calculate the percent yield on a weight basis:

$$\% \text{ Yield} = (W_2/W_1) \times 100$$

where:  $W_1$  = the initial weight of oil or fat

$W_2$  = the final weight of the finished biodiesel

$$\% \text{ Yield} = \underline{\hspace{2cm}}$$

- b. Calculate the average molecular weight of the ethyl esters using the known MW's of oil, ethanol and glycerol and the relationship below:

$$MW_{oil} + 3 \times MW_{ethanol} = 3 \times MW_{ethyl\ ester} + MW_{glycerol}$$

$$Avg MW_{ethyl\ ester} = \underline{\hspace{2cm}}$$

## Laboratory 6: Physical and Chemical Solubility

### *Topics Covered*

- Physical solubility
- Chemical solubility
- Like dissolves like
- Polarity

### *Equipment Needed (per pair or group)*

- Weighing scale (readable to 0.01 g)
- bunsen burner
- ring stand, ring and wire gauze
- 4 test tubes, 20 ml
- tube holder and rack
- 2 thermometers
- graduated cylinder
- marker (for labeling test tubes)
- glass stirring rod
- 250 ml beaker

### *Reagents Needed (per pair or group)*

- 20 grams potassium nitrate

### Background Information -- Physical Solubility

Solubility can be a fairly complex subject. Basically you have a solute (gas, liquid or solid) that mixes with or dissolves in a solvent (usually a liquid) to form a homogeneous solution. The amount of solute that can be dissolved in the solvent is called the solubility of that particular solute in that particular solvent. For example, the solubility of sugar (sucrose) in water is about 2 grams/mL at room temperature. That's a lot, considering one mL of water weighs only 1 gram.

Sucrose is a molecular solid with the formula  $C_{12}H_{22}O_{11}$ . A clump of sugar is made up of thousands of individual molecules held together by weak intermolecular forces or bonds. When it dissolves in water, the bonds are broken and individual molecules are released (dissociate from one another) into the water (equation 1). When enough sugar has been added to reach the solubility level it is said to be saturated, meaning no more sugar will go into solution.



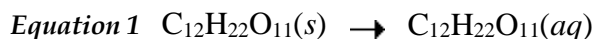
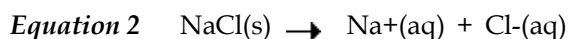


Table salt or sodium chloride (NaCl) is an ionic solid that dissociates into its positive and negative ions when dissolved in a liquid (see equation 2). The solubility of salt in water at room temperature is about 0.3 grams NaCl/g H<sub>2</sub>O.



Solubility is temperature and pressure dependent. Generally, as the temperature and pressure increase, the solubility of one substance in another will increase. For example the solubility of sugar in hot water can go up to as much as 5 grams/g of water (see figure 1). The solubility graph for NaCl vs. temperature is fairly flat but does increase slightly from 0 to 100°C.

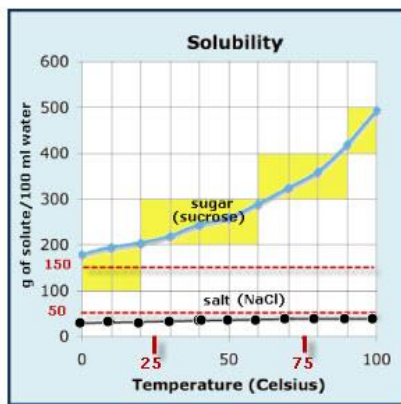


Figure 1. Solubility vs. temperature of sugar and salt in water.

Solubility can be expressed in units of concentration, molality, mole fraction, mole ratio, and other units. Once the solubility limit or saturation is achieved, the solute will begin to precipitate out as more is added or if the solution begins to cool. Solubility levels can range from infinitely soluble (miscible) such as ethanol in water, to insoluble such as oil and water. Technically a small amount of water is soluble in oil.

A useful rule of thumb for predicting solubility is "like dissolves like," meaning a solute will dissolve best in a solvent that has similar chemical characteristics. One of these characteristics is polarity. A highly polar solute like sugar is very soluble in highly polar water, less soluble in fairly polar methanol, and insoluble in non-polar hexanes. Similarly, non-polar oil is very soluble in non-polar hexanes, less soluble in fairly polar methanol, and insoluble in very polar water.

The term hydrophilic, meaning “attracted to water,” is somewhat synonymous to polar. Polar molecules are hydrophilic and are typically charged and capable of hydrogen bonding, enabling them to dissolve in water. Non-polar molecules are hydrophobic, “afraid of water,” and generally do not dissolve in water or other polar solvents. Some molecules have characteristics of both. Soap, for example, is a long molecule that has a polar head and a non-polar tail, allowing it to dissolve in both water and oil. As you may know, it is very useful for cleaning non-polar oil and grease off your hands with polar water.

## Background: Chemical Solubility

A solution can be formed through dissolution, but it can also be formed because of a chemical reaction. This is what distinguishes chemical solubility from physical solubility as in the sugar or salt in water examples. The process of making biodiesel gives us several examples of chemical solubility.

For example, a catalyst is generally needed for the transesterification reaction for making biodiesel. One of the typical catalysts used for this is prepared by dissolving sodium hydroxide (NaOH) in methanol. The resulting solution is the product of a chemical reaction between the NaOH and the methanol that forms sodium methyllate and water.



The biodiesel reaction between methanol and triglycerides (oils and fats) goes through different stages of solubility between the reactants and the products of reaction (methyl esters and glycerol). Initially methanol is not soluble in oil. However, as the reaction begins, mono and diglycerides as well as methyl esters are formed and act as co-solvents to allow the methanol and oil to become soluble in each other. As the reaction progresses, free glycerol is produced, which is not soluble in the methyl esters.

Also a side reaction occurs, which produces some soap. You end up with two phases: the lighter phase contains a solution of mostly methyl esters, some methanol, a little soap, and very little glycerol. The heavy phase contains a solution of mostly glycerol, some methanol, some soap, and very little methyl esters. The methanol, which is somewhat polar, will dissolve in both the non-polar esters and the polar glycerol. The soap (which has properties of both) is responsible for a little glycerol in the ester phase and a little of the esters in the glycerol phase.

## Pre-Lab Questions

- How is the solubility of sugar in water affected by increasing the temperature?
- What does the phrase “like dissolves like” mean?
- How is solubility expressed?

- What is the difference between a saturated and an unsaturated solution?

**Safety Note:** Potassium nitrate can irritate the eyes, skin, and lungs. Wear eye protection, gloves, a mask, and a lab coat when handling this chemical.

## Laboratory Procedure

1. Number four test tubes and place in rack.
2. Weigh  $\text{KNO}_3$  and water into the four tubes as indicated in table 1.

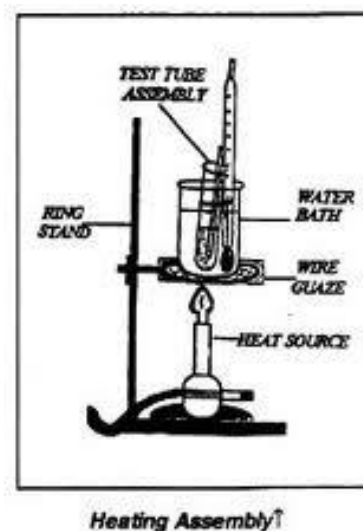
Table 1

Tube #	$\text{KNO}_3$ , g	DI water, mL
1	2	5
2	4	5
3	6	5
4	8	5

3. Prepare a water bath by filling a 250 ml beaker  $\frac{3}{4}$  full of water. Place on ring stand as shown in figure 2 and heat to  $90^\circ\text{C}$ .
4. Place each test tube in turn or all 4 together in the water bath and stir with a glass stir rod until the  $\text{KNO}_3$  is dissolved.
5. Take each one out of the bath in turn along with a hot, dry thermometer placed into the solution and observe the first sign of crystallization as it cools. Record the temperature in table 2.

Table 2

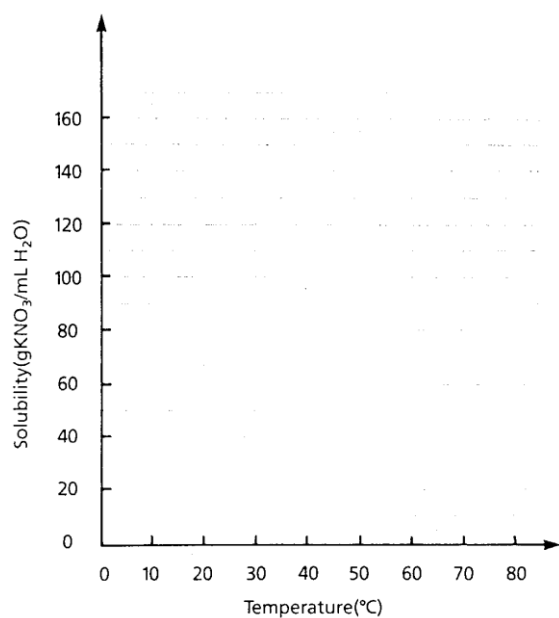
Tube #	$\text{KNO}_3/\text{H}_2\text{O}$	Crystallization temp $^\circ\text{C}$
1	2g + 5mL	
2	4g + 5mL	
3	6g + 5mL	
4	8g + 5mL	



## Data Processing

Now you are going to use the information you discovered to draw a solubility vs temperature curve. The Y axis (solubility) is often expressed in grams of solute / 100mL  $\text{H}_2\text{O}$ . First convert your data into (g  $\text{KNO}_3$ :100mL  $\text{H}_2\text{O}$ ) ratio. As an example a 2:5 ratio would equal a 40:100 ratio. Next, plot your data and draw the solubility curve for  $\text{KNO}_3$  vs. temperature.

# Biodiesel Fundamentals for High School Chemistry Classes



## Laboratory 7: Using Differences in Solubility to Remove Contaminants from Biodiesel

### *Topics Covered*

- Solubility
- Polarity
- Like dissolves like
- Partition Ratio

### *Equipment Needed (per pair or group)*

- One graduated titration burette with stand, 50 mL
- 3 Erlenmeyer flasks, 250 mL each
- Separatory funnel, 500 mL (if available)
- Pipette
- Weighing scale (readable to 0.01 g)

### *Reagents Needed (per pair or group)*

- 120 mL unwashed biodiesel
- Distilled or de-ionized water
- Isopropyl alcohol, anhydrous
- 1% phenolphthalein solution in isopropyl alcohol
- 0.1 N Hydrochloric acid

### **Background Information**

When triglycerides are mixed with methanol and catalyst, a reaction occurs, and two phases separate. The top portion is biodiesel. The glycerol portion settles to the bottom, and contains most of the catalyst, soap, and excess methanol.

However, even after the glycerol settles out, the biodiesel is contaminated with some methanol, residual glycerol, soap, and catalyst. If this contaminated biodiesel is used in an engine, it could damage the engine by leaving ash deposits, or even prevent the engine from running by plugging fuel filters.

How can these contaminants be removed from the biodiesel? The contaminants that are dissolved in biodiesel will dissolve more readily in water, because the contaminants and water are both “polar,” whereas biodiesel is not very polar. Therefore, we can remove the contaminants by mixing the biodiesel with water, and then letting the water settle out. This is often referred to as “washing” the biodiesel.

## Polarity

A molecule that is polar has a negative end and a positive end—kind of like a magnet, which has a north pole and a south pole. Water is an example of a highly polar molecule: the oxygen side is negatively charged, and the hydrogen side carries a positive charge.

Polar substances dissolve easily in water because when water comes into contact with other polar molecules, the negative end of the water molecule attracts the positive end of the other molecule, and the positive end of the water molecule attracts the negative end of the other molecule.

Because water is very polar and biodiesel is not very polar, the two do not dissolve in each other. When a biodiesel-water mixture is allowed to sit undisturbed, the water (with some of the contaminants) will settle out at the bottom of the container and can then be removed.

Polarity is a matter of degree. Contaminants that are strongly polar, such as glycerol, will be strongly attracted to water and almost completely insoluble in biodiesel. Methanol, on the other hand, is polar enough to be soluble in water but is also partially soluble in biodiesel. The attraction of a compound to different solvents can be characterized by the partition ratio.

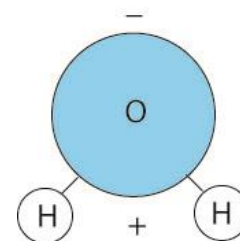
## Partition Ratio

Even though the polar contaminants will dissolve fairly easily in the water, less than 100% of each contaminant will be removed with the water wash. Because biodiesel is slightly polar, some percentage of each contaminant will remain with it. Each time the biodiesel is washed, more and more contaminants will be removed.

How many times do you need to wash the biodiesel in order to reduce the contaminants to an acceptable level? This question can be answered by measuring the partition ratio of each contaminant.

The partition ratio,  $P$ , is shown in this equation:

$$P = \frac{[X]_1}{[X]_2}$$



The concentration of a substance called  $X$  in solvent 1 is expressed as  $[X]_1$ . The concentration of a substance is often shown by using square brackets. By convention, the concentration in the organic, or non-polar, phase goes on top. The aqueous, or polar, phase goes on the bottom.

The partition ratio is the ratio of the concentrations of a given substance in two different solvents (in this case, biodiesel and water). For example, if after washing the biodiesel, there is 10 times more of a particular contaminant ( $X$ ) in the wash water than in the biodiesel, the partition ratio

for X is  $1/10$ , or 0.1. This means that each time we wash the biodiesel, the amount of X in the biodiesel goes down by a factor of 10.

Remember that the concentration is the number of moles of a substance in some volume, usually a liter, of a solvent. So, if we take 1.2 moles of KOH (MW=67.3g) and add enough water to make one liter of solution, we have a concentration of 1.2 moles/liter.

In this laboratory, we will measure the partition ratio for potassium hydroxide (KOH) as it partitions between water and biodiesel. Potassium hydroxide is commonly used as a catalyst for biodiesel production.

## Pre-Lab Questions

1. If 40 g of KOH is dissolved into 500 mL of water, what is the concentration of KOH?
2. Why does biodiesel have to be washed more than once to remove contaminants?
3. Why will typical biodiesel contaminants dissolve more readily in water than in biodiesel?

**Safety Note:** In this lab you will be using isopropyl alcohol, which is flammable. Keep it away from heat or flames. The biodiesel you will be working with is contaminated with potassium hydroxide, a caustic chemical which can harm skin and eyes. Wear goggles and gloves when handling the contaminated biodiesel.

## Laboratory Procedure

1. Weigh an approximately 20 g sample of biodiesel to an accuracy of 0.01 g and transfer this biodiesel to the titration flask. Record the sample size in Table 1.
2. Measure the amount of catalyst present in the biodiesel sample by titrating with 0.1 moles/liter of HCl, using the procedure below:
  - a) Add 125 mL of isopropyl alcohol into the flask containing the biodiesel sample.
  - b) Add a couple of drops of phenolphthalein indicator solution into the biodiesel solution. The solution should turn pink, which indicates that the solution is basic.
  - c) Swirl the solution for approximately 1 minute to ensure the uniformity of the solution.
  - d) Fill the burette with the known concentration HCl and water solution.
  - e) Record the starting volume of titrant in Table 1.
  - f) Carefully add the titrant from the burette into the flask while swirling the solution to mix. Do not allow the solution to splash.
  - g) When the solution starts to turn from pink to very light pink, add the titrant slowly, drop-by-drop. Stop introducing titrant when the solution changes completely to clear.
  - h) Record the ending volume of titrant in the data table.
  - i) Subtract the ending volume from the starting volume to get the volume of titrant added.
  - j) Calculate the amount of KOH using the following equation:

$$\frac{\text{moles KOH}}{\text{g sample}} = \frac{(\text{mL titrant}) \times (\text{normality of titrant})}{1000 \times (\text{weight of sample})}$$

- Now you will wash some biodiesel. Place about 100 mL of unwashed biodiesel into a 500 mL separatory funnel. Add an equal volume of distilled or de-ionized water (room temperature) to the biodiesel. Agitate gently by rocking the funnel back and forth for two minutes. Do not shake!
- Let the water separate for 5-10 minutes. Save the washed biodiesel and separated wash water.
- Take a 20 g sample of this washed biodiesel in a 250 mL flask. Weigh and record the weight to an accuracy of 0.01 g. Measure the catalyst again using the titration method described above in Step 2. Record the data on Table 2.
- Take a 20 g sample of the wash water (saved from Step 4) in a 250 mL flask. Weigh and record the weight to an accuracy of 0.01 g. Measure the catalyst in the wash water by repeating Step 2. Record the data on Table 3.
- To calculate the partition ratio, the measured values of KOH in moles of KOH/g must be converted into concentrations (moles/liter). To do this, multiply the moles of KOH/g by the density of the solutions (biodiesel = 870 g/liter and water = 1000 g/liter).

$$[X_{\text{moles/liter}}] = \text{density}_{\text{g/liter}} \times [X_{\text{moles/g}}]$$

- Record the converted concentration in moles/liter from Tables 2 and 3 into Table 4.
- Calculate the partition ratio by using the following formula:

$$P = \frac{[X_{\text{biodiesel, moles/liter}}]}{[X_{\text{water, moles/liter}}]}$$

- Record the calculated the partition ratio into Table 4.

## Data Recording and Processing

Table 1 Data recording of unwashed biodiesel

Unwashed biodiesel	Category	Quantity	Results
	Sample size	Flask weight (g)	
		Flask + sample (g)	
		Net sample size (g)	
	Titrant volume	Starting volume (mL)	
		Ending volume (mL)	
		Net volume (mL)	
	KOH concentration	moles/gram	

Table 2 Data recording of washed biodiesel

Washed biodiesel	Category	Quantity	Results
	Sample size	Flask weight (g)	
		Flask + sample (g)	
		Net sample size (g)	
	Titrant volume	Starting volume (mL)	
		Ending volume (mL)	
		Net volume (mL)	
	KOH concentration	moles/gram	

Table 3 Data recording of wash water

Wash water	Category	Quantity	Results
	Sample size	Flask weight (g)	
		Flask + sample (g)	
		Net sample size (g)	
	Titrant volume	Starting volume (mL)	
		Ending volume (mL)	
		Net volume (mL)	
	KOH concentration	moles/gram	

Table 4 Data recording for partition ratio calculation

No.	Category	Data Source	Results
1	Raw biodiesel	Concentration in moles/g (from Table 1)	
2		Concentration in moles/liter (converted from Step 7)	
3	Washed biodiesel	Concentration in moles/g (from Table 2)	
4		Concentration in moles/liter (converted from Step 7)	
5	Wash water	Concentration in moles/g (from Table 3)	
6		Concentration in moles/liter (converted from Step 7)	
7	Partition ratio	Calculated from Step 8 (ratio of line 4 to line 6 -- dimensionless)	

Questions:

1. Does KOH dissolve better in a polar solvent or a non-polar solvent? Explain your answer.
2. If we used glycerol to wash the biodiesel instead of water, do you think the glycerol would remove the KOH from the biodiesel?

## Laboratory 8: Density Measurement of Chemicals and Fuels

### Topics Covered

- Density as a physical property of chemical compounds
- Changes in density based on temperature
- Determining densities of pure chemicals and mixture/blends of methyl esters and diesel fuel, such as methanol, glycerol, vegetable oils, methyl esters, and diesel

### Equipment Needed (per pair or group)

- Three 150 mL measuring cylinders
- Weighting scale to measure 100 g of chemicals
- A glass bulb thermometer or a thermocouple

### Reagents Needed (per pair or group)

- Vegetable oil – approximately 150 mL
- Biodiesel made from the same oil as above – approximately 150 mL
- Petroleum diesel – approximately 100 mL

### Background Information – Density

The density of a substance is defined as mass per unit volume. Density is a way of quantifying how heavy or light a substance is for a given amount of volume. Mathematically:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} \quad (8.1)$$

Example:

If 1 L of vegetable oil weighs 930 g, the density of the oil can be calculated as:

$$\text{Density} = 930 \text{ g}/1000 \text{ mL} = 0.93 \text{ g/mL}$$

The mass of a substance is the sum of the masses of all individual molecules. Therefore, the density of a substance can be changed by changing the number of molecules occupying a unit volume. For instance when a substance is heated, the heat energy increases the molecular vibration, pushing tightly packed neighboring molecules farther apart. As a result, a given number of molecules occupies more volume without increasing its mass. Therefore, from equation 8.1, when volume increases without increasing the mass, the density decreases.

Therefore the density of a substance is somewhat temperature dependent. Usually the density is decreased with increasing temperature. There may be other factors that affect the intermolecular

distance other than temperature, and hence general density-temperature relation may not hold. One such example is the density of water, which is highest at 4°C.

When two substances are mixed together, several things could happen. Let's imagine mixing substance A with substance B. If the intermolecular distance of substance A is large enough that substance B can snugly fit into the void, the density of the mixture will be higher than that of substance A. Imagine pouring some sand into a bucket of gravel. The sand will fill in the spaces between the pieces of gravel, and hence the density of the mixture of sand and gravel is greater than that of gravel alone.

This also holds true when a chemical compound is dissolved. For example, quite a lot of sugar or salt can dissolve in water without increasing the water volume. The process increases the density of the chemical mixture. This is the reason sea water is about 2.5% heavier than fresh water.

The density of a mixture with two components can be calculated as:

$$\text{Mixture Density} = \frac{\text{Mass of A} + \text{Mass of B}}{\text{Mixture Volume}} \quad (8.2)$$

If all of component B can fit into the voids of component A, then the mixture volume is essentially the same as the volume of component A. It is worth noting that when component B fits into the voids of component A, the mixture density is always greater than component A, but not necessarily greater than the density of component B. This is because the mixture volume is usually greater than the volume of component B. Imagine a sponge with some water sprinkled onto it. The mixture density will be higher than the density of the dry sponge, but less than the density of water.

In the second type of mixture, the voids are not big enough for substance A to accommodate substance B. In this case the mixture volume in equation 8.2 is the sum of the volume of the individual components. A mixture of atmospheric gases (such as nitrogen and oxygen) is an example.

In the third type of mixture, component A chemically reacts with component B and the product of the reaction may have lower or higher density, depending on the chemical reaction. The density of the product depends on the chemical structure of the molecule formed.

The density of matter in the gaseous phase can be calculated mathematically from its molecular formula. However, the density of liquids and solids is not as straightforward as that of gases. One mole of gas always occupies 22.4 L at standard temperature (0° C) and pressure (1 atm). Therefore the density of a gas at standard temperature and pressure can be calculated as:

$$\text{Density of gas} = \frac{\text{Molecular weight of the gas in grams}}{22.4} \text{ g/L} \quad (8.3)$$

## Pre-Lab Questions

1. Why does the density of a substance usually decrease at higher temperatures?
2. What is the density of CO<sub>2</sub> at standard temperature and pressure (STP)?  
(The molecular weight of CO<sub>2</sub> = 44)

**Safety Note:** In this lab you will be handling petroleum diesel. Use gloves and an apron when handling this chemical, because it can irritate skin, and also can cause an odor that is difficult to remove from skin and clothes.

## Laboratory Procedure

1. Calculate the mass of methanol needed, and how much biodiesel and glycerol are produced, from 100 mL of soybean oil reacted. The biodiesel transesterification is given by the following chemical reaction:

1 mole of triglyceride + 3 moles of methanol → 3 moles of biodiesel + 1 mole of glycerol

### Given:

Average molecular weight of soybean oil = 872.33 g/mol

Molecular weight of methanol = 32.04 g/mol

Average Molecular weight of biodiesel = 292.12 g/mol

Molecular weight of glycerol = 92.09 g/mol

2. Now calculate the mass of the chemicals required to react with approx. 100 g of soybean oil to 0.01 accuracy. Since 3 moles of methanol are required for each mole of soybean oil, the mass of the methanol reacted with 100 g of oil is given by:

$$\text{Mass of the methanol} = \frac{3 \times \text{Molecular weight of methanol}}{\text{Molecular weight of soybean oil}} \times 100 = \text{_____}g$$

Similarly, the mass of biodiesel produced and glycerol can be calculated as:

$$\text{Mass of the biodiesel} = \frac{3 \times \text{Molecular weight of biodiesel}}{\text{Molecular weight of soybean oil}} \times 100 = \text{_____}g$$

$$\text{Mass of the glycerol} = \frac{\text{Molecular weight of glycerol}}{\text{Molecular weight of soybean oil}} \times 100 = \text{_____}g$$

## Measurements

# Biodiesel Fundamentals for High School Chemistry Classes



- Take the temperatures of the soybean oil, biodiesel and petroleum diesel and ensure that they are all at room temperature. If not wait until they all come to room temperature.
- Pour weighed mass (weight in grams) of soybean oil in a measuring cylinder using a dropper and a weighing scale.
- Pour calculated mass (weight in grams) of biodiesel in a separate measuring cylinder using a dropper and a weighing scale.
- Pour 50 g of petroleum diesel in the third measuring cylinder using a using a dropper and a weighing scale.

Observe the volume of biodiesel fuel produced compared to the volume of the soybean oil used to make the fuel. Note down your observations along with following measurements.

Volume of the soybean oil used to make biodiesel = \_\_\_\_\_mL

Volume of biodiesel produced = \_\_\_\_\_mL

Volume of petroleum diesel = \_\_\_\_\_mL

Now carefully pour biodiesel into petroleum diesel until the mixture weights 100 g. Measure the volume of the fuel mixture.

Volume of the fuel mixture = \_\_\_\_\_mL

## Data processing

Calculate the density of the soybean oil, biodiesel and petroleum diesel

Soybean oil Density = \_\_\_\_\_g/L

Biodiesel Density = \_\_\_\_\_g/L

Petroleum diesel Density = \_\_\_\_\_g/L

Biodiesel and Diesel Mixture Density = \_\_\_\_\_g/L

Biodiesel to oil ratio in mass basis = \_\_\_\_\_g of biodiesel/g of oil

Biodiesel to oil ratio in volume basis = \_\_\_\_\_mL of biodiesel/mL of oil