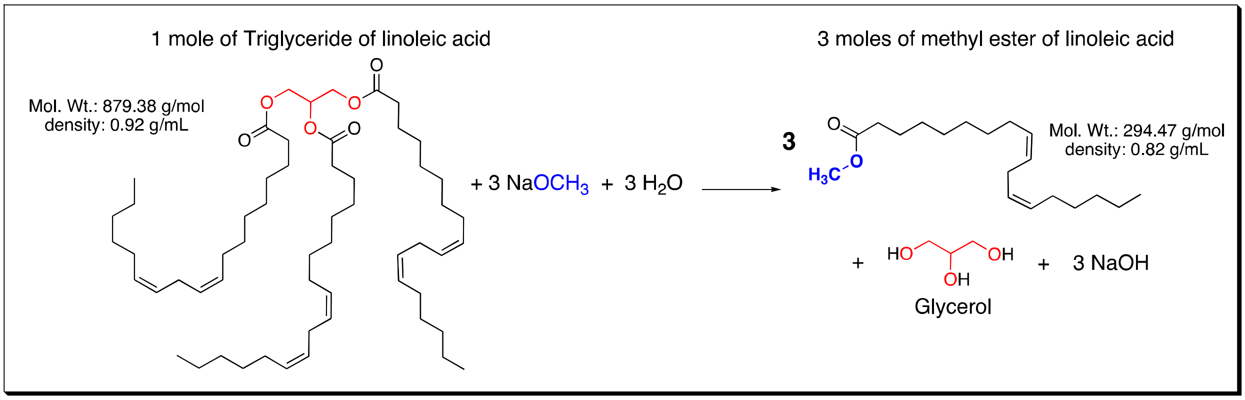
Experiment 7 - A Small Scale Synthesis of Biodiesel

Biodiesel has gained a lot of attention over the past decades because of its use as an alternative to fossil fuels for automobiles and trucks. Biodiesel consists of the methyl esters of fatty acids found in vegetable oil, obtained through a process called **transesterification** (see **Scheme 1** below).[1] The combustion of biodiesel releases carbon dioxide gas into the atmosphere similar to the combustion of fossil fuels. However, biodiesel is viewed as being more carbon-neutral than fuels obtained from petroleum products because the carbon in plant-derived biodiesel originated from carbon dioxide in the atmosphere.



Scheme 1. Synthesis of biodiesel from corn oil *via* "transesterification."

There are many cars and light duty pick-up trucks on the market today engineered to operate using multiple fuel sources, including biodiesel. More commonly, people purchase kits that enable them to convert their own gasoline-powered cars to run on biodiesel. Many of these people make their own biodiesel at home, procuring the vegetable oil from restaurants in their community. This re-purposing of used cooking oil converts an industrial waste product into a usable commodity, providing additional validation for the use of biodiesel as an alternative to fossil fuels.

In this experiment, students will synthesize biodiesel from a commercially available vegetable oil.[2,3] Products will be observed and analyzed by ^{1}H NMR. The source of the oil indicates the types of fatty acids present and whether those fatty acid chains contain one or more *cis*-alkenes (**Tables 27.1** and **27.2**).

Table 27.2 Composition of Some Fats and Oils

	Saturated fatty acids (%)				Unsaturated fatty acids (%)	
Source	C_{12} lauric	C_{14} myristic	C_{16} palmitic	C_{18} stearic	C_{18} oleic	C_{18} linoleic
Animal fat						
Lard	—	1	25	15	50	6
Butter	2	10	25	10	25	5
Human fat	1	3	25	8	46	10
Whale blubber	—	8	12	3	35	10
Vegetable oil						
Coconut	50	18	8	2	6	1
Corn	—	1	10	4	35	45
Olive	—	1	5	5	80	7
Peanut	—	—	7	5	60	20

J. McMurry, *Organic Chemistry, 8th edition*

Table 27.1 Structures of Some Common Fatty Acids

Name	No. of carbons	Melting point (°C)	Structure
Saturated			
Lauric	12	43.2	$CH_3(CH_2)_{10}CO_2H$
Myristic	14	53.9	$CH_3(CH_2)_{12}CO_2H$
Palmitic	16	63.1	$CH_3(CH_2)_{14}CO_2H$
Stearic	18	68.8	$CH_3(CH_2)_{16}CO_2H$
Arachidic	20	76.5	$CH_3(CH_2)_{18}CO_2H$
Unsaturated			
Palmitoleic	16	−0.1	(Z)-$CH_3(CH_2)_5CH{=}CH(CH_2)_7CO_2H$
Oleic	18	13.4	(Z)-$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$
Linoleic	18	−12	(Z,Z)-$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6CO_2H$
Linolenic	18	−11	(all Z)-$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6CO_2H$
Arachidonic	20	−49.5	(all Z)-$CH_3(CH_2)_4(CH{=}CHCH_2)_4CH_2CH_2CO_2H$

Notebook Preparation

- *Purpose:* One-sentence description of the experimental and learning objectives, in addition to the reaction scheme (**Scheme 1**).
- *Reagent table*: List the amounts (mg or mL and mmol), molar equivalents ("equiv."), and physical properties (MW, bp or mp, density, one-word hazard) of each chemical in the reaction scheme.
- *Procedure* (remote) – hand-drawn 'comic strip' with diagrams or flow chart including all equipment, chemicals with amounts, and safety hazards or precautions. Include pertinent notes from the Clean-up & Safety Table.

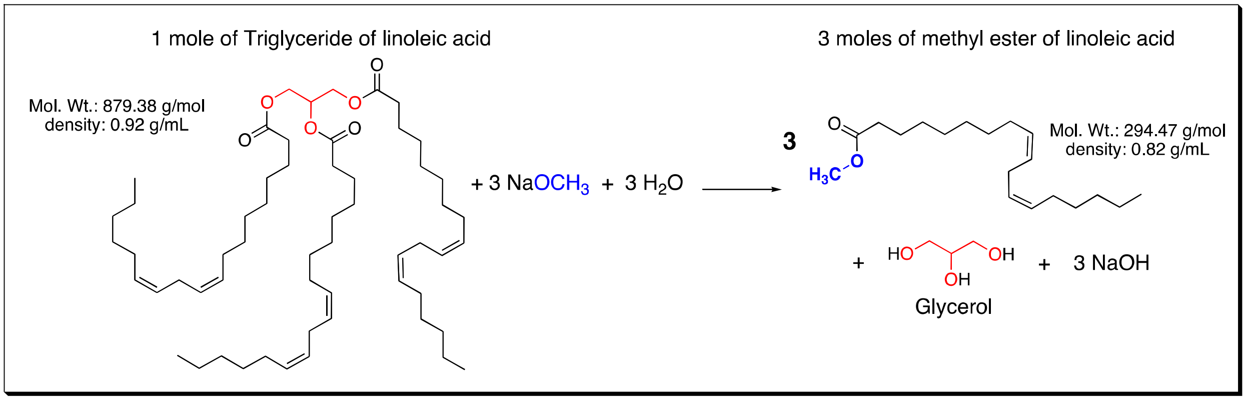
EXPERIMENTAL PROCEDURE[2,3]

Step A: Preparation of sodium methoxide ($NaOCH_3$) solution (Eq 1)

$$NaOH + CH_3OH \rightarrow NaOCH_3 + H_2O \qquad (1)$$

This solution should be prepared in a fume hood. Weigh 1 pellet of NaOH (approximately 0.10 g) and transfer it into a mortar. Use a pestle to grind the NaOH pellet into a fine powder. NaOH is hygroscopic, caustic, and will cause burns on contact so use caution. To facilitate the transfer of the NaOH powder, pour 1.5 mL of methanol into the mortar. Methanol is flammable and poisonous and should be handled with care. Use the pestle and/or a glass stir rod to break the NaOH powder free from the interior of the mortar so that it can dissolve into the methanol. Transfer as much of the contents as possible to a 50 mL round-bottom flask using a glass funnel and stir rod to control the flow of liquid. *Remember this is a very basic and caustic solution!* Clean up any spills immediately with a spill mat. Add 1.5 mL more methanol into the mortar to dissolve any remaining NaOH and transfer it to the RBF (for a total of 3 mL MeOH). Add a magnetic stir bar to the flask and use a stirring hot plate to gently stir the mixture at room temperature for 5-10 minutes (or until the NaOH has dissolved) as you begin Step B.

Step B: Transesterification reaction



1 (Triglyceride) + 3 $NaOCH_3$ + 3 H_2O → 3 (methyl ester of fatty acids) + 3 NaOH + 3 Glycerol **(2)**

Use a graduated cylinder to measure 12 mL vegetable oil and add it to the $NaOCH_3$ solution prepared in step A. Attach a water-jacketed condenser and reflux the solution in a boiling water bath for 20 minutes. Since there is not enough water pumps to be used at the hoods for reflux, it is extra important that ice cold water is running through the condenser at all times. The solution must be stirred vigorously so that the mixture of methanol and vegetable oil does not separate into two layers. Once the reflux is complete, remove the heat but allow the solution to cool before handling the flask.

Step C: Isolation & Analysis

Transfer the crude reaction mixture to a large test tube while the solution is still a little bit warm but not hot. Allow the test tube to sit for 5-10 minutes undisturbed. Record observations regarding the appearance of the products in comparison to the starting materials (color, viscosity, etc.). Analysis will be primarily through observation. Exact yield will not be determined, but volumes are estimated by visually comparing similar amounts of water in another test tube.

Students will prepare samples for NMR analysis to represent as many different oils as possible. Add 2 drops of biodiesel to 800 µL $CDCl_3$ directly in the NMR tube per TA demo. Use a long-stem pipet to mix the solution. Do not invert the NMR tubes, as the caps are not spill proof! Add a paper label to the sample (no tape) with the following: "Last Name, First Initial, Section Day/Time, TA, Vegetable Oil ID." Spectra will be posted online with special focus on methyl ester protons, alpha protons, and any vinylic protons.

Step D: Waste disposal & Clean up Procedure

Incorporate into notebook pages

Dispose of the products in liquid waste. Wash all glassware at least twice with hot water (if you can get it) and lots of soap. Thoroughly clean all countertops with the cleaner provided (spray bottle) and dry with a paper towel. Do not leave greasy counter-tops please!

References

1. Leung, D. Y. C.; Wu, X.; Leung, M. K. H. *Appl. Energy,* **2010**, *87*, 1083−1095.

2. Meyer, S. A.; Morgenstern, M. A. *Chem. Educator*, **2005**, *10 (2)*, 130-132.

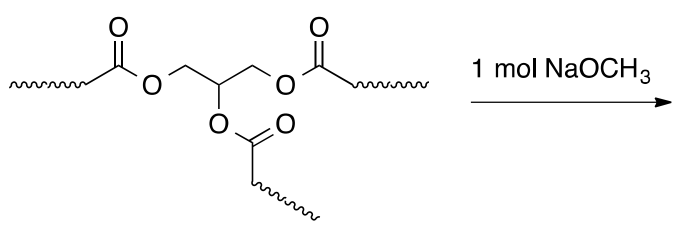
3. Yang, J.; Chunli, X.; Li, Baozin, L.; Ren, G.; Wang, L. *J. Chem. Ed.* **2013**, *90*, 1362-1364.

PRE-LAB QUESTIONS

1) What is the difference between a saturated fat and an unsaturated fat? How is an unsaturated fat different from a poly-unsaturated fat? Be able to identify an example of each from its common name or structure (Tables 27.1 – 27.2).

2) Identify the intermolecular forces (IMFs) present in triglycerides, methanol, glycerol, and biodiesel.

3) Draw the arrow-pushing mechanism and products of the reaction of a triacylglycerol with just one mole of $NaOCH_3$.



4) Calculate the mmols of methanol and the vegetable oil from the amounts given in the procedure. Show your work. Determine the limiting reagent. What is the mole ratio in the balanced equation?

5) Calculate the theoretical yield of biodiesel in mmol and milliliters. Show your work.

LAB REPORT

IN-LAB QUESTIONS

1) Report the physical observations and approximate yield (mL) of biodiesel. Calculate the percent yield. Show your work.

2) The analysis of the ^{1}H NMR spectrum will not be very detailed, as the long chains cause many peaks to overlap. Instead, create a table with the observed peaks with chemical shift range (beginning to end of signal). *Assign only the distinctive peaks* outside of the alkyl region to the best of your ability. Include the structure of the methyl ester and label accordingly.

3) Report your observations of the products in comparison to the starting materials (methanol and vegetable oil) and to each other (glycerine and biodiesel).

> **(a)** Use IMFs to explain why biodiesel is immiscible with methanol, glycerol, and water.
>
> **(b)** Students used to work up this transesterification in a separatory funnel. This was very time and temperature sensitive. It can take several minutes for the glycerol and biodiesel layers to separate from the emulsion. As the glycerol cools, it begins to solidify and becomes difficult if not impossible to drain out of the funnel through the stopcock. **Use IMFs to explain why glycerol causes this stopcock blockage**.

4) Briefly describe one method that could have been performed in the lab to purify the biodiesel product.

Experimental Methods

Refer to Writing Guidelines on experimental methods on Canvas and sample questions from the Experiment 1 PDF. Remember this is a *very abbreviated form of the procedure*. It will help to make a list of each chemical used in the reaction and workup, including the amount in g or mL and mmol. The yield of biodiesel should be reported as an approximate volume along with the % yield from vegetable oil. Overlapping ^{1}H NMR signals can be reported as a range and/or multiplet.