Waste Vegetable Oil and Titrations: Teacher Manual

Goals

- Understand how the frying process alters the composition of vegetable oil.
- Understand why titration is performed on WVO before introducing it to the transesterification reaction.
- Understand how to perform a titration.
- Understand why additional base is added to the transesterification reaction.

Objectives

- Students will perform multiple titrations on samples of WVO.
- Students will use their results to calculate the amount of additional base needed to neutralize FFAs in the WVO.
- Students will product biodiesel from WVO.
- Students may be involved in the WVO collection and pre-treatment processes.

Materials

- Waste vegetable oil (WVO)
- Large container for heating oil
- Stove burner or hot plate
- Sock filter(s)
- Scale(s)
- KOH
- Weigh boats
- Distilled water
- 1.5 L beaker
- Funnel

For each student group:

- 1 burette
- 3 small (50 ml) flasks
- 1 graduated pipette
- Phenolpthalein pH Indicator
- 60-mL Isopropyl alcohol
- 10-ml graduated cylinder
- Small funnel

Preparation and procedures

The process of converting waste vegetable oil (WVO) to biodiesel is essentially the same as that of converting virgin vegetable oil, but working with WVO requires a few extra steps:

1. Collection
2. Filtration
3. Heating and settling
4. Titration
5. Calculating the amount of additional base catalyst

Collection

To convert WVO to biodiesel, oil must first be collected from a deep fryer. The first step in collecting WVO is to establish a relationship with your provider. If you have fryers at your school, it should be easy enough to collect enough oil for a classroom experiment. We encourage students to be involved in this process.

The Biodiesel Program currently collects WVO from cafeterias on campus, major universities in Chicago, all of the museums in Chicago, and from local restaurants. Kitchens often change fryer oil on a regular schedule, so you should be aware of this as you prepare the lesson. A system or protocol for pick-up may need to be established. We leave collection pails with the cafeterias on campus, and our restaurant providers typically return the fryer oil to its original vessel once it has cooled. **Caution: Never collect hot oil.**

Filtration

The frying process often introduces food particles to the oil, and the oil must be filtered before undergoing the transesterification reaction. We typically pre-filter the oil through a 100 micron sock filter. Old t-shirts make a good, quick substitute for sock filters. The filtration process should be performed in advance of a transesterification reaction, and we encourage the involvement of students in this process.

Heating and Settling (Optional)

In addition to food particles, foods introduce water to the fryer oil. We pre-heat our WVO to 70°C which allows water (and additional food particles) to settle to the bottom of the vessel. Excess water and solid material will settle on the bottom of the oil container. Pre-heating should be started at least one day before a transesterification reaction.

Titration

WVO is typically more acidic than virgin vegetable oil. When foods containing water are fried in hot oil, some of the water reacts with triglyceride molecules to form free fatty acids (FFAs) (Fig 1). FFAs are fatty acid molecules that are not bound to glycerin. These acids react with the base catalyst to form soap (Fig 2), effectively leaving less catalyst available for the transesterification of triglycerides to biodiesel. The result is a less complete transesterification reaction.

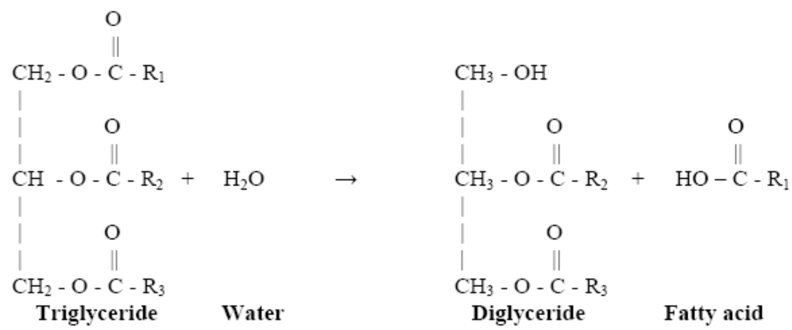

Fig 1. Hydrolysis of a triglyceride to form a free fatty acid (from Van Gerpen et al 2004)

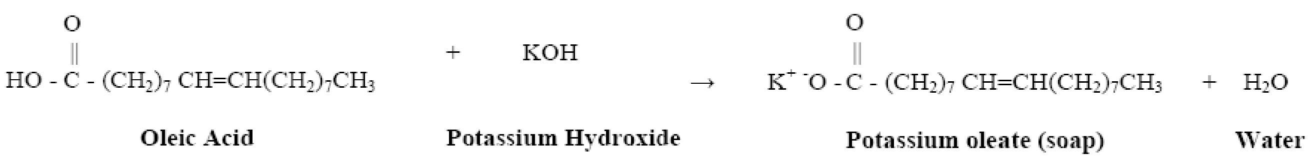

Fig 2. Formation of soap from oleic acid (an FFA) (from Van Gerpen et al 2004)

FFAs, however, can be neutralized simply by adding additional base catalyst so that they don't interfere with the transesterification reaction. In this case, FFAs are intentionally converted to soap. (Subsequently, this method is impractical for oils with very high FFA content.) To determine the amount of additional catalyst, one must determine the acid content of the WVO. This can be accomplished by titration.

Titration allows one to determine the concentration of acid in a known volume of WVO by neutralizing it with a reference solution (or *titrant*) of known base concentration in the presence of a pH indicator. The following titration procedure has been popularized among biodiesel homebrewers for its ease of use. Conveniently, the number of milliliters of reference solution needed to neutralize the analyte corresponds directly with the grams of additional base needed per liter to neutralize the FFAs in the WVO. The process is as follows:

Preparing the reference solution

This basic solution of known concentration will allow determination of the acid concentration of the WVO in the analyte. This recipe prepares a 0.1% KOH solution. The reference solution can be prepared either in advance by the teacher or during the lab by the students.

1. Dissolve 1 g of KOH in 1 L of distilled water (or tap water if purified water is not available).
2. Pour the reference solution into a burette.

Preparing the analyte: *Student Procedure*

1. Using a graduated cylinder, measure 20 ml of isopropyl alcohol.
2. Pour the isopropyl alcohol into a 50 ml flask.

3. Add 2-3 drops of phenolphthalein solution to the alcohol.
4. Swirl to mix.
5. Add 1 ml of WVO. Swirl until thoroughly mixed (you should start to see the oil bubbles disassociate and begin to mix with the isopropyl).
6. Repeat steps 1-5 two more times. You will need three separate flasks of analyte.

Titration procedure: *Student Procedure*

1. Place a flask under the burette containing reference solution.
2. Record the initial volume of reference solution in the burette.
3. Slowly add reference solution (one drop at a time) to the analyte solution.
4. Swirl the beaker between each addition.
5. Continue to add reference solution to the oil/alcohol solution until it turns pink and stays pink for ~30 seconds while swirling.
6. Stop.
7. Record the quantity of reference solution used, where V_0 is initial volume, V_f is final volume, and T is total volume of reference solution:

$$T = V_0 - V_f$$

8. Repeat titration procedures for each flask.
9. Calculate the average value for T ($\bar{T}$) from the three trials.

Calculating the amount of additional base catalyst: *Teacher Procedure*

1. Either assign a volume of WVO for reactions by students, or have them determine the quantity of WVO appropriate for their jar (remember that you will also need to add methanol and lye).
2. Have students determine the quantities of base and methanol needed to react with your WVO.

Biodiesel Ingredients and Proportions

Using Waste Vegetable Oil

_____ L feedstock oil (*Hint:* 1 gal = 3.79 L)

_____ mL methanol = 0.2$*$ ***x*** L of oil $*$ 1000

_____g KOH = (8.5 g KOH + $\bar{T}$) $*$ ***x*** L of oil

Making Biodiesel from WVO

At this point, students can proceed with the transesterification reaction as outlined in the Biodiesel Program “Making Biodiesel from Virgin Vegetable Oil” lab activity with the addition of the extra base that they have calculated.

Questions:

1). If the WVO were to contain a higher number of free fatty acids, how would that affect the amount of base used in the reaction? Why?

- *It would require the addition of more base to neutralize the acids. If additional base is not added, the conversion of FFAs to soap will make less base catalyst available to the transesterification reaction, and an incomplete conversion of vegetable oil to biodiesel will result.*

2) Why is it important to perform the titration three times and use the average *T* value?

- *Repeating trials and using an average value minimizes the chances of experimental error in determining the* T *value.*

3) Why is it more important to perform titration when using WVO than when using virgin vegetable oil?

- *WVO is more likely to have a high FFA content, due to the application of high heat and the introduction of water, which causes the hydrolysis of triglycerides to FFAs.*

References:

Van Gerpen, J., B. Shanks, R. Pruszko, D. Clements, and G. Knothe. 2004. *Biodiesel production technology.* National Renewable Energy Laboratory. Golden, CO.

Waste Vegetable Oil and Titrations: Student Lab

Ever been waiting behind a bus, bus driver hits the gas, and all of a sudden you're hungry for French fries? Well, if that hasn't happened to you yet, it will. We're going to turn this French fry grease into fuel! Waste to energy! Unfortunately, as you might notice, used fryer oil is often pretty cruddy. That's why it's getting thrown away. Fortunately, with a few steps, we can make waste vegetable oil (WVO) suitable for conversion to biodiesel fuel.

Background:

First, we have to get this crud out of the WVO. Much of this crud is food particles left in the oil. Technically, these food particles are called chunkles®, and by technically we mean we made up that word. How are we going to get the chunkles® out of there? You got it – a chunkle® filter! The Biodiesel Program uses a 100 micron chunkle® filter to filter our oil before processing it. No filter? No problem, just use an old t-shirt!

Second, most food stuff contains water. When food is fried, it introduces water to the oil. We can separate most of the water from the oil by gently heating the oil to about 70°C, which causes the water to settle to the bottom. Now why does that happen? And once it's there how do we remove it from the oil? These are the kinds of problems faced by people trying to save the planet.

Additionally, the chemical composition of vegetable oil changes when it is used in a deep fryer. The combination of water and heat causes the vegetable oil (triglyceride) molecules to break apart and form fragments called free fatty acids (FFAs). FFAs will react with the base catalyst to form soap. Soap! When this reaction takes place, it uses up catalyst that was intended to convert triglycerides into biodiesel, and we don't get a complete conversion of WVO to biodiesel. So, we have to add more than 8.5 g of KOH per liter of oil to neutralize the extra acid in WVO. This will turn the FFAs into soaps, and still leave plenty of catalyst for the transesterification reaction.

But how much additional KOH do we have to add? (Another problem faced by somebody trying to save the planet.) Fortunately, chemists have devised a simple technique to address this problem. It's called *titration.* In our case, titration can be used to determine the amount of extra base required to neutralize the FFAs. Titration is based on the idea that one molecule of base will neutralize one molecule of acid.

So, if we know the amount of base required to neutralize a sample of oil, we should know the amount of acid in the oil. Additionally, if we know how much basic *reference solution* (or *titrant*) was required to neutralize the solution (or *analyte*) that contains the oil, we should know how much additional base catalyst we need to add to our reaction to neutralize the FFAs in the oil. In this titration, the milliliters of reference solution you use will correspond directly to the additional grams of base catalyst you need to add to the reaction.

When we do our titrations, we need to know when all of the acid in the oil has been neutralized. We can use a pH indicator to help us determine when this has happened. In this lab, we'll use a pH indicator called *phenolphthalein,* which turns pink in a basic solution.

When performing a titration, you will drip the reference solution into the analyte until the color of the solution just begins to turn pink and remains pink after gently swirling for about 30 seconds. You will then record the amount of reference solution added. When making biodiesel from WVO, the Biodiesel Program uses the following recipe:

For every 1 L feedstock oil (WVO) use:

0.2 L methanol (CH_3OH)

8.5 g KOH + $\overline{T}$

(where $\overline{T}$ = *average milliliters of reference solution used in titration to neutralize the analyte)*

Laboratory safety

Put on safety goggles and gloves.

Procedure:

Preparing the reference solution

This basic solution of known concentration will allow determination of the acid concentration of the WVO in the analyte. This recipe prepares a 0.1% KOH (or NaOH) solution.

1. Dissolve 1 g of KOH in 1 L of distilled water or isopropyl alcohol.
2. Pour the reference solution into a burette.

Preparing the analyte

1. Using a graduated cylinder, measure 20 ml of isopropyl alcohol.
2. Pour the isopropyl alcohol into a 50 ml flask.
3. Add 2-3 drops of phenolphthalein solution to the alcohol.
4. Swirl to mix.
5. Add 1 ml of WVO. Swirl until thoroughly mixed (you should start to see the oil bubbles disassociate and begin to mix with the isopropyl).
6. Repeat steps 1-5 two more times. You will need three separate flasks of analyte.

Titration procedure

1. Place a flask under the burette containing reference solution.
2. Record the initial volume of reference solution in the burette.
3. Slowly add reference solution (one drop at a time) to the analyte solution.

4. Swirl the beaker between each addition.
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Calculating the amount of additional base catalyst

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Making Biodiesel from WVO

You are now prepared to make biodiesel from waste vegetable oil! Proceed as you would with virgin vegetable oil, but be sure to add the extra base catalyst that you've calculated based on your titration results.

Questions:

1). If the WVO were to contain a higher number of free fatty acids, how would that affect the amount of base used in the reaction?

2) Why is it important to perform the titration three times and take the average T value?

3) Why is it more important to perform titration when using WVO than when using virgin vegetable oil?