"Homebrew" Oil Titration

Materials:

- Volumetric Flask
- Balance (accuracy of 0.01g)
- Stir Plate
- Ring stand
- Burette
- Burette holder
- 3ml plastic Pipette
- 25mL Beakers
- Graduated Cylinder
- Distilled H_2O
- KOH (100% purity)
- Isopropyl Alcohol
- Phenolthalien (pH indicator)
- Oil or Fat

Procedure:

1. Make Titration solution - Tit*ration solution may be stored in airtight container for up to 3 months of use.*
    a. Measure 500mL distilled H2O using volumetric flask
    b. Transfer h2O into 1L Erlenmeyer flask
    c. Using balance, weigh 0.5g KOH
    d. Add KOH to flask containing H2O
    e. Place stir bar in flask and put on stir plate, cover, and stir until KOH is completely dissolved
    f. Transfer solution to properly labeled squeeze bottle for use
2. Fill burette with .1% KOH solution (record amount of solution in burette)
3. Using a graduated cylinder, measure 10mL isopropyl alcohol and add to 25mL beaker
4. Using a 3mL plastic pipette, measure 1mL oil and add to isopropyl alcohol
5. Add 5-7 drops phenolthalein in alcohol/oil mixture
6. Stir while adding .1% KOH solution to alcohol/oil mixture until flashes of pink begin to appear
7. Slowly add (short squirts or single drops) .1% KOH solution until the alcohol/oil mixture turns pink and holds color for 10-15 seconds. Record remaining amount of .1% KOH remaining in burette
8. Subtract remaining KOH solution from original amount and record. This is what we will refer to as the *titration number*.

Analysis:

1. ***Convert*** the number of milliliters used to titrate the oil into grams of KOH – this is your titration number
    Example: *Titration requiring of 5.7mL of titrate solution would be equivalent to 5.7g KOH*
2. ***Calculate*** amount of KOH needed for reaction using the equation:
    (9.0g KOH + Titration Number) X Liters to be reacted = Total grams KOH for reaction
    Example: You have found that the oil you are to process has a *titration number* of 2.4 mL and you would like to use .5L of oil in reaction. The equation in this instance would be:
    (9.0g KOH + 2.4g KOH) X .5L = ***5.7g KOH***

Biodiesel Mini-Batch ("Homebrew" Equation)

Materials:

- Stir plate
- Stir bar
- 1L Mason Jar
- Balance (accuracy of 0.01g)
- Warm Water Bath
- 500mL Separatory Funnel
- Graduated Cylinder
- 1 quart Mason Jar

Reagents:

- Potassium Hydroxide (100% purity)
- 55mL methanol
- 250mL Oil or Fat

Procedure:

3. Measure 250ml oil in graduated cylinder, add oil to mason jar, and heat in warm water bath to 120^0F
4. Calculate the *titration number* of the oil to be processed using the Homebrew Titration procedure.
5. Convert the number of milliliters used to titrate the oil into grams of KOH
   Example: *Titration number of 5.7mL would be equivalent to 5.7g KOH*
6. Calculate amount of KOH needed for reaction using the equation:
   (9.0g KOH + Titration Number) X Liters to be reacted = Total grams KOH for reaction
   Example: You have found that the oil you are to process has a *titration number* of 2.4 mL and you would like to use .5L of oil in reaction. The equation in this instance would be:
   (9.0g KOH + 2.4g KOH) X .5L = ***5.7g KOH***
   In this example we would be using 500mL of oil, 110mL methanol, and 5.7g KOH in the reaction
7. **Under Hood -** Measure 55mL of methanol and put into 1 quart Mason jar.
8. **Under Hood** - Weigh catalyst and carefully add to methanol. Shake until KOH is completely dissolved. (You have now created potassium methoxide)
   Important: Work quickly but carefully to replace cap of catalyst container. KOH will absorb moisture from air and become a solid block if allowed to sit in open container.
   Important: Potassium methoxide is extremely corrosive. Always use care when handling methoxide and should always be handled under the fume hood.
9. Once oil has reached 120^0F, remove 1 Liter Mason jar from water bath and place it under the fume hood next to methoxide. Add methoxide to oil and tightly replace lid of jar.
10. Vigorously shake Mason jar for 60 seconds and then place back into warn water bath for 30 minutes.
11. **Under Hood** -Transfer contents of mason jar into 500mL separatory funnel, cap with stopper, and let sit overnight.

Residual Catalyst & Soap Titration

Explanation:

Production of biodiesel using an alkali catalyst always produces some amount of soap. There will be more soap with recycled restaurant waste and animal fats and less with refined vegetable oils.

After the transesterification reaction is complete, the leftover catalyst and soap tend to concentrate in the glycerol phase. However, some soap and a small amount of catalyst may be left in the biodiesel phase. During process development, it can be useful to know the amount of soap formed, where the catalyst resides, and how effective the washing process is in removing these two compounds.

In the first titration, the HCl neutralizes the alkali catalyst, so when the phenolphthalein indicates that the solution has become neutral, then all of the catalyst has been counted. Then, if the titration is continued, the HCl, as a strong acid, begins to split the soap molecules to free fatty acids and salt. When the pH reaches about 4.6, where the bromophenol blue changes color, then this indicates that the HCl has split all of the soap. It is now lowering the pH, so it has protons to donate since the soap has all been split.

Materials:

Balance (0.01g accuracy)
Ring Stand
10mL Burrette
Stir Plate & Stir Bar
250mL Beaker
Pippette

Reagents:

Isopropyl Alcohol or Acetone
Phenolthalien (0.1%)
Bromophenol Blue (0.04%)
Hydrochoric Acid (0.1N Solution)

Procedure:

1. Measure 100ml of Isopropyl Alcohol in 250ml beaker.
2. Add 10g of unwashed esters to isopropyl alcohol. Place beaker on stir plate and begin stirring.
3. Add 10ml of 0.1N HCL to burrette
4. Add 5 drops of phenolthalien to alcohol/ester solution. If solution turns pink, add HCL until solution looses pink color. Record amount of HCL required to change solution color as "A"
   This represents the amount of residual catalyst in your esters.
5. Add 20 drops of bromophenol blue to alcohol/ester solution. Add HCL to solution until it turns a bright yellow and holds color. Record amount of HCL required to change solution color as "B".

Analysis:

Residual Catalyst

Now, the amount of HCl added during the first titration tells us how much free catalyst is in the sample and the amount added during the second titration tells us the amount of soap.

If you take the ml of HCl added for the first titration and do the following calculation:

["A" ml of 0.1 N HCl] x [1 liter/1000 ml] x [0.1 moles of HCl/liter] x [1 mole of KOH/mole of HCl] x [56.1 g/mole KOH] / [grams of sample] = grams of KOH/gram of sample or

$$\frac{A \times 0.1 \times 56.1}{1000 \times W} = \text{grams of KOH catalyst / grams of sample}$$

This gives the amount of free catalyst in the sample, done here assuming the catalyst was KOH. You can substitute the appropriate molecular weight for other catalysts (KOH =56.1, NaOH = 40.0, NaOCH3 = 54.0).

Soap Content

To calculate the amount of soap in ester sample use the equation:

$$\frac{B \times 0.1 \times 320.56}{1000 \times W} = \text{grams of soap / grams of catalyst}$$

- *B* is the number of ml of HCl required to turn ester sample from blue to yellow.
- *W* is the weight of the ester sample used in the titration.
- 320.56 is used if ester sample was reacted using KOH as catalyst, if NaOH is
- used, 304.4 should be substituted in the equation.
- To convert results to parts per million (ppm), multiply result by 1,000,000.

This often expressed as ppm, so this number should be multiplied by one million. This calculation assumed the soap was potassium oleate. When using sodium catalysts, the molecular weight of sodium oleate is 304.4 g/mole.

27/3 Conversion Test

Explanation:
The 27/3 test can be used as a qualitative assessment of conversion. Due to the insolubility of triglycerides in methanol, any unconverted triglycerides will not be miscible in methanol and thus will precipitate to the bottom of the centrifuge tube. In general, if no precipitate is seen at the bottom of the tube the fuel being tested has been well converted.

Materials:
50 ml Centrifuge tube

Reagents:
Methanol
Methyl Esters

Procedure:

1. Measure 27ml of methanol and pour into centrifuge tube.
2. Add 3ml of methyl esters to centrifuge tube.
3. Securely place cap on centrifuge tube and invert 2-3 times. **Do not shake.**
4. Hold centrifuge up to light source and watch for falling droplets.
5. Allow mixture to settle for 5-10 minutes.
6. Inspect tip of centrifuge tube for precipitate.

Analysis:

If no precipitate is visible upon inspection, the fuel has been well converted.

If precipitate is observed, conversion has not been taken to completion.

Courtesy of CCCC Biofuels Program