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.

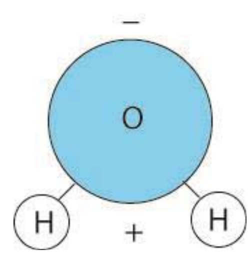
Because water is very polar and biodiesel is not very polar, the two do not dissolve in each other. When a biodiesel-water mixture is allowed to sit undisturbed, the water (with some of the contaminants) will settle out at the bottom of the container and can then be removed.

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:

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

3. 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!
4. Let the water separate for 5-10 minutes. Save the washed biodiesel and separated wash water.
5. 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.
6. 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.
7. 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).

$$[X_{moles/liter}] = density_{g/liter} \times [X_{moles/g}]$$

8. Record the converted concentration in moles/liter from Tables 2 and 3 into Table 4.

9. Calculate the partition ratio by using the following formula:

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

10. Record the calculated the partition ratio into Table 4.

Data Recording and Processing

Table 1 Data recording of unwashed biodiesel

	Category	Quantity	Results
Unwashed biodiesel	**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

	Category	Quantity	Results
Washed biodiesel	**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

	Category	Quantity	Results
Wash water	**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?