Background

Distillation

Many organic compounds are liquid at room temperature. If a reaction results in a mixture of miscible liquids, the separation of the liquids requires a new technique known as distillation. Distillation uses the different boiling points of liquids in a mixture to separate the components.

Concept of Distillation

Many organic compounds are volatile, which means they have relatively high vapor pressures and low boiling points. Distillation uses this volatility by boiling the liquid mixture in a single flask and condensing the vapors that travel into the apparatus, allowing a liquid to be collected at the other end. As long as there is a difference in boiling points between the liquids in the mixture, one component will distill over before the other.

Pure organic compounds will distill over a very narrow boiling point range. If the boiling point range or distilling range is too wide, the collected compound is likely impure and a complete separation was not obtained. However, not all compounds with narrow boiling point ranges are pure. An azeotrope is a mixture of two liquids which has a constant boiling point and composition throughout distillation. An example azeotrope is a mixture of ethanol and water; ethanol has a boiling point of 78.4 ^{o}C and water has a boiling point of 100 ^{o}C but a mixture of 95% ethanol and 5% water has a boiling point of 78.1 ^{o}C .When distilling ethanol and water, the collected ethanol will be 95% with 5% water due to the azeotrope.

Boiling point depends on atmospheric pressure, which is not likely to be 760 torr, and thus the observed boiling point is not the normal boiling point of the liquid. If the final boiling point does not exactly correspond to the literature boiling point, it is most likely due to the pressure and/or the thermometer, and not to “operator/experimental error” or some impurity in the remaining mixture.

Addition of Fractionating Column

There are many types of distillation that differ in the components of the distillation apparatus. All distillation set-ups do have similarities, though. A simple distillation has the most basic set-up of the distillation options. The flask with the mixture is attached to some form of condenser, which empties into a new container. The set-ups also include a thermometer to monitor the vapor temperature compared to the expected boiling points. All set-ups must also be open to a gas environment in some way, whether that is open to air or another gas. A closed distillation system could allow the pressure to build up and cause an explosion.

An important refinement of the basic technique is fractional distillation, which adds a fractionating column to give better separation of liquids with similar boiling points. The fractionating column is included right above the heated flask, as shown in Figure 1. The column contains extra surfaces

on which the high boiling point component can condense back to liquid into the flask, releasing heat that helps vaporize the low boiling point component and move it through the system.

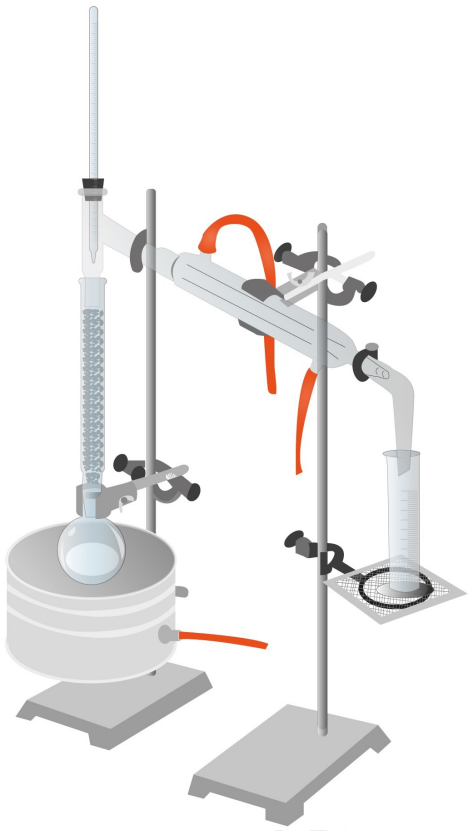

Figure 1 Fractional distillation set-up with fractionating column above the sample flask

Fractional distillation allows for a better separation of liquids with a boiling point difference of 40 degrees or less. Consider the plot in Figure 2 following the distillation of two liquids with boiling points of 81 degrees and 110 degrees.

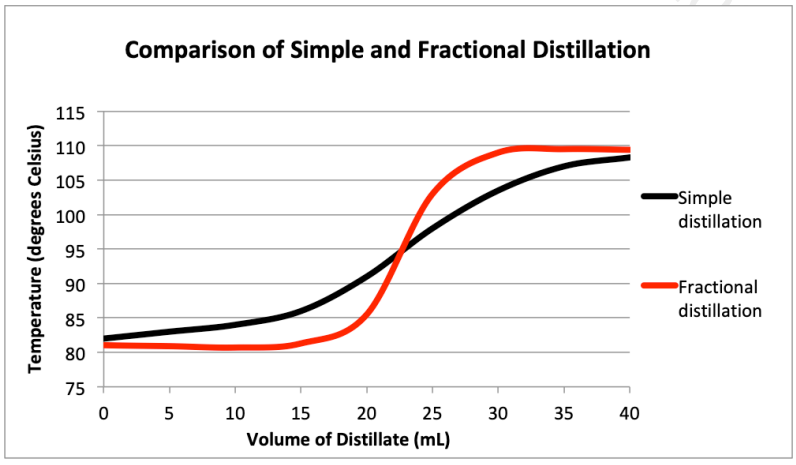

Figure 2 Comparison of simple and fractional distillation temperature behavior over a distillation

There is no sharp transition in the black line representing the temperature behavior during the simple distillation, indicating that there is a wide range of collected distillate containing a mixture of both liquids. The red line has a much sharper transition, which indicates a cleaner separation between the two liquids.

Objectives

- Explore the procedure and benefits of fractional distillation
- Conduct a fractional distillation on a mixture of ethyl acetate and butyl acetate

Materials

- Fractional distillation set-up
- Ethyl acetate/butyl acetate mixture
- Test tubes
- Boiling chips
- Vials for GC analysis

> *Ethyl acetate and butyl acetate are both flammable. There must be no flames or sparking sources present in the laboratory during this experiment.*
>
> *Have your instructor check the set-up before heating.*
>
> *Never heat a closed system and never distill to dryness.*

Procedure

Performing the Fractional Distillation

You will work as a pair of students to collect the data. Each pair will measure the temperature ranges and volumes of the fractions obtained during the distillation. Each pair should also save their first, last and a middle fraction in vials for gas chromatographic analysis.

1. Begin by securely clamping the 50 mL-round-bottom distilling flask to a ring stand.
2. Place about 20 mL of the ethyl acetate/butyl acetate mixture of unknown volume composition and 2 or 3 small boiling chips in the round bottom flask. Make sure you record the volume in the graduated cylinder precisely, e.g. 19.7 mL.
3. Assemble the rest of the distillation apparatus. Insert the fractionating column between the distilling flask and distilling head. The distillate fractions are collected in test tubes ("fraction collectors") immersed in an ice bath. When assembling the glass pieces of your distillation apparatus it is advisable to clamp the glassware pieces to each other (using keck-clamps) as you proceed.
4. Begin a gentle flow of water from the tap to the water inlet of the condenser. Connect another rubber hose to the condenser outlet and run the water down the cup drain in the center of your lab station.
5. **When your pair is ready to begin the distillation, have your instructor inspect your set-up before you proceed.**
6. Slowly heat the distillation flask with a heating source as designated by the instructor. Regulate the heating so that the condensate collects slowly and steadily, without interruption, approximately 1 drop/sec.
7. During the distillation, collect and measure the volume that accumulates during a temperature change of 5 degrees in each test tube. For example, the first test tube should

hold the distillate collected between room temperature and 70 ºC, and the second test tube should hold the distillate collected between 70 and 75ºC. If there is a dramatic change of the head temperature (1 degree per second), change the receiving test tube. Record approximately how many drops were collected, and then begin your five-degree intervals again when the temperature levels off.

8. Measure the volume of each fraction using a small graduated cylinder. After measuring each volume in a test tube, turn the graduated cylinder upside down on a paper towel that is crumpled in the bottom of a beaker to allow the cylinder to drain between volume measurements. Measure as accurately as possible because your final results will depend upon it.
9. Continue the distillation until about 1- 2 mL of liquid remains in the pot. CAUTION: **Do not distill to dryness**. Remove the heat source and turn off the heat. Allow the liquid in the column to drain into the distillation pot; measure and record the volume of this pot residue.
10. Describe the distillation process with regard to temperature changes in your notebook.
11. Save a middle fraction and the two fractions that you believe to be pure ethyl acetate and pure butyl acetate in Teflon lined, screw-cap vials for gas chromatographic analysis in a later lab period. *Remember to record in your notebook the temperature ranges for the fractions you have saved.*

Analyzing the Fractional Distillation

The additive fraction volumes should approximately equal the volume of the mixture initially used. Remember, the pot residue is included because it was part of the initial mixture and you should be able to deduce its composition.

Plot the line graph (not scatter plot) for volume of distillate (y-axis) collected in each temperature range *versus* the temperature range (x-axis). Make sure to include your pot residue as part of your high boiling fraction. Begin your temperature axis at about 4-5 degrees prior to the actual distillation temperature. An example chart is shown in Figure 3; your graph should resemble the red line from the figure. If you collected some distillate over some irregular temperature intervals (<5 deg. or > 5 deg.), please write correction notes directly on your graph. It is not easy to put these non-regular intervals in a line graph.

After plotting the data, inspect the resulting graph. It should somewhat resemble a gas chromatogram. The principle of separation on the basis of boiling point is the same in both the GC and distillation procedures. You should be able to tell fairly clearly the areas of the graph that correspond to (mostly) ethyl acetate distilling and to (mostly) butyl acetate distilling since you know their respective boiling points. On this basis, decide what parts of the graph (fractions) are primarily ethyl acetate, primarily butyl acetate, and a mixture of the two.

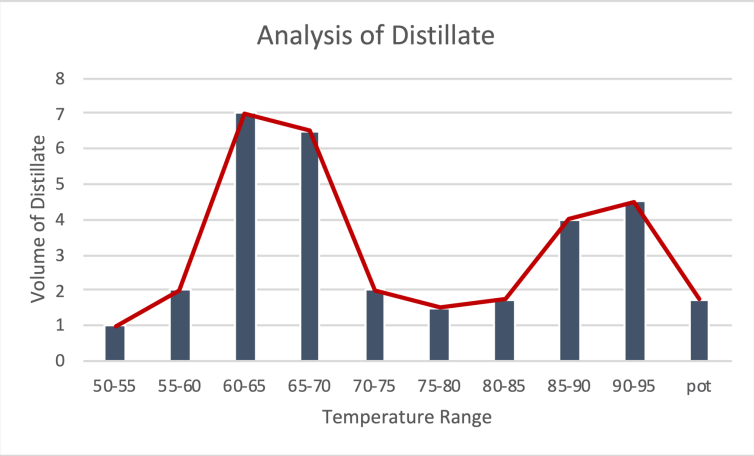

Figure 3 A two-component mixture that has been separated by distillation. The boiling points of the two pure components are 64° and 92°. The volumes collected between ~70° and ~85° are a mixture of the two components.

If there is not a clear separation of the mixture, you will have to make some assumptions about the composition of the volume that was not clearly separated. These assumptions will need to be explained and supported. On the graph itself, clearly designate which part of the total [distillate fractions + pot residue] you will use for the estimation of ethyl acetate and which part is used for the estimation of butyl acetate. All distillation fractions and pot residue must be designated as ethyl acetate, butyl acetate, or a mixture of both.

When you have decided how much of the total recovered volume is ethyl acetate and how much is butyl acetate, calculate the volume percent composition of each of the two components in the unknown mixture. The volume percentages should add up to 100% and must include all the recovered volumes in the calculation.

After you have determined the volume percent composition, use literature values for density and molar mass, you can convert to mole percent composition.

Pre-Lab Questions

Prepare for lab by completing and understanding the answers to these questions. Refer to the Background or another resource, such as your textbook, if necessary.

1. What are the boiling points of ethyl acetate and butyl acetate in the mixture?

2. What precautions should you take when setting up a distillation apparatus?

3. Completely describe the benefit of including a fractionating column in a distillation.

4. What is an azeotrope?

5. What is the basis of the separation being performed in this experiment?

Fractional Distillation Report Sheet

Name _____ Lab section _____

Date _____ Instructor _____

Performing the Fractional Distillation

Preparing for the distillation

Ethyl acetate lit. boiling point (°C) _____

Butyl acetate lit. boiling point (°C) _____

Initial volume of sample (mL) _____

Distillate collection

Temperature Range (°C)	**Fraction Volume (mL)**
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

Ending the distillate collection

Pot residue volume (mL) _____

Total volume recovered (mL) _____

Percent recovery _____

Analyzing the Fractional Distillation

Complete the graph of your distillation data as described in the procedure. On the chart itself, clearly mark which volume areas you will use for the calculation of % ethyl acetate, which areas you will use for the calculation of % butyl acetate, and which area is a mixture of the two. The pot residue (which would have distilled if you had let it), must be included.

	Temperature Range (°C)	**Volume (mL)**
Fractions assumed to be mostly ethyl acetate	_____	_____
Fractions assumed to be a mixture	_____	_____
Fractions assumed to be mostly butyl acetate	_____	_____
Total volume of fractions		_____

Percent composition calculations

	Volume % composition
Ethyl acetate	_____
Butyl acetate	_____

	Molar mass (g/mol)	Density (g/mL)	Mole % composition
Ethyl acetate	_____	_____	_____
Butyl acetate	_____	_____	_____

Post-Lab Questions

1. Explicitly state which volumes are likely a mixture of the two components. What percentage of the mixture volume is likely to be EtOAc and BuOAc? Explain your reasoning.

2. Explain what is meant by "efficiency" with respect to a distillation. Comment on the efficiency of your fractional distillation as seen by your graph.