Organic Chemistry Techniques

This experiment is divided into several parts:

Part 1: Distillation, Micro-boiling points and Gas Chromatography (GC)
Part 2: Column Chromatography and Thin Layer Chromatography (TLC)
Part 3: Extraction, Isolation, and Recrystallization

This experiment is a compilation of some of the most common techniques used in Organic Chemistry. It may be difficult to use the GC when you would like. Therefore, do the distillations first, and use a GC when it is free. Always use the same GC. You may do the other parts of the experiment in the order that you choose.

Part 1: Distillation, Gas Chromatography & Micro-Boiling Point

Background

Distillation is a common method for purifying organic liquids. It involves an initial vaporization, which separates a compound from its less volatile contaminates, followed by a condensation of the "pure" distillate, which is collected. There are various types of distillation, and the method used will often depend on the boiling point of the compound to be isolated, and the specifics of the desired separation. For example, *simple distillation* can separate two mutually soluble substances, which differ in boiling points by 80°C or more. On the other hand, *fractional distillation* can separate two compounds, which boil within 25°C (or more) of one another. For extremely high boiling liquids, or those that decompose at high temperature, vacuum *distillation* is often used. In this case, the distillation apparatus is sealed from the atmosphere and connected to a vacuum source (a water aspirator or a vacuum pump). The boiling point of a liquid is the temperature at which the vapor pressure of that liquid is equal to the applied pressure. So, the vacuum reduces the applied pressure within the apparatus, thereby reducing the temperature at which the liquid boils.

In this experiment, you will attempt to separate a 40:60 mixture of hexanes and toluene by both simple and fractional distillation. You should compare the two methods, and determine the effectiveness of each by analyzing the distillates using gas chromatography.

A. Simple Distillation

The temperature of a distillation process over time depends, in part, on the vapor pressure of the liquid being distilled. The vapor pressure of the liquid depends, in part, on the liquid's composition. For a pure liquid, the vapor above the liquid and the liquid itself will be in thermal equilibrium throughout the distillation. As a result, the distillation proceeds at a relatively constant temperature (Figure 1A; page 2).

However, for any liquid mixture, the composition of the vapor in equilibrium with the heated solution will be different from the composition of the solution itself. In addition, the composition of both the liquid and the vapor will change during the distillation. As a result, the temperature increases throughout the distillation. (Figure 1B & C). Two laws of physical chemistry, as defined below, describe this behavior:

- Dalton's Law: the vapor pressure of a liquid is the sum of the partial pressures of the individual components: $P = P_A + P_B$

- Raoult's Law: at a given temperature and pressure, the partial pressure of a compound in a mixture is equal to the vapor pressure of the pure compound times its mole fraction in the mixture: $P_A = P_A^{pure} \times X_A$

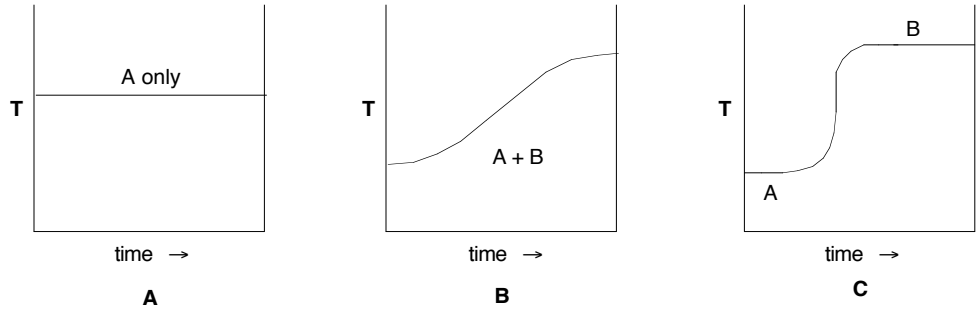


Figure 1: Temperature Behavior During Simple Distillation. A: a relatively pure compound; B: a mixture of two components having similar boiling points (< 80°C); C: a mixture of two components with widely differing boiling points (> 80°C).

A **phase diagram** is a plot of composition (mol %) vs. temperature (T), where the lower curve is the liquid line and the upper curve is the vapor line (Figures 2 & 3). These diagrams

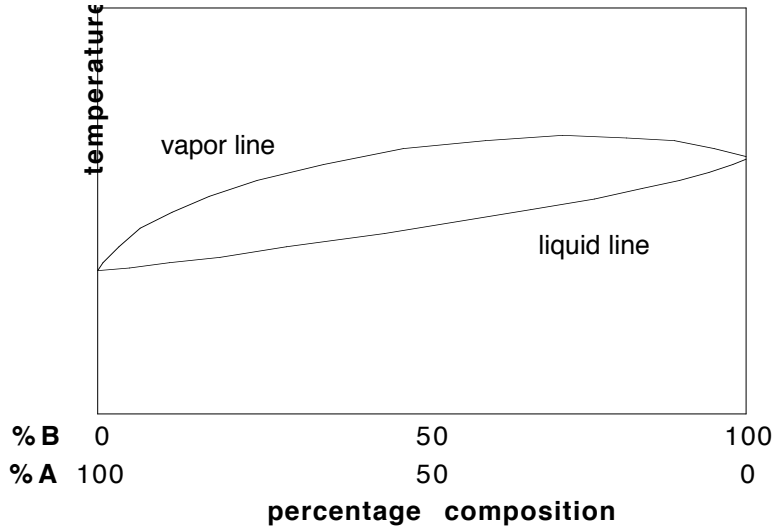


Figure 2: Phase diagram for a mixture of two components having similar (< 80°C) boiling points (*cf.* Figure 1B).

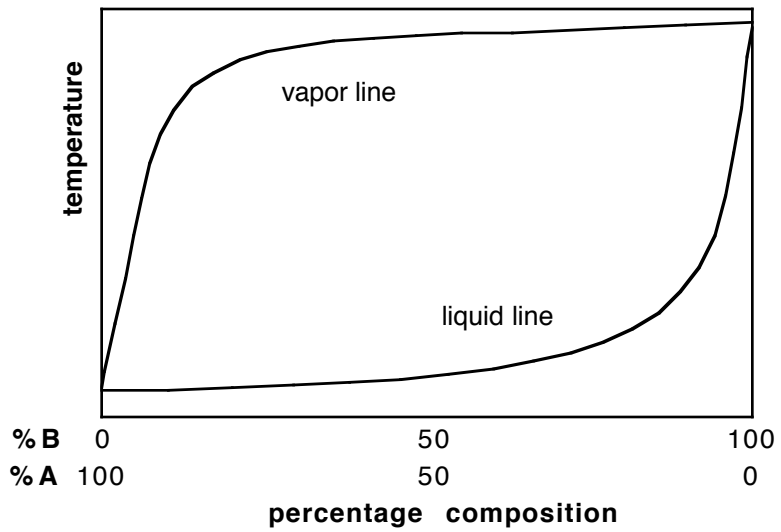


Figure 3: Phase diagram for a mixture of two components having widely varied (> 80°C) boiling points (*cf.* Figure 1C).

help to explain the temperature vs. time behavior (Figure 1) of liquid mixtures, and additionally can be used to determine the composition of both the liquid and the vapor at any temperature throughout the distillation.

B. Fractional Distillation:

The physical principles that describe a simple distillation are also true for fractional distillation (Figure 4). In this case, however, as the vapor passes up through the fractionating column it undergoes a continuous cycle of condensation and revaporization. Each revaporization is equivalent to a simple distillation. Thus, the composition of the vapor is progressively enriched as it moves up the column (Figure 5, following page). In this way, it is possible to separate cleanly components of liquid mixtures in which the boiling points differ by more than

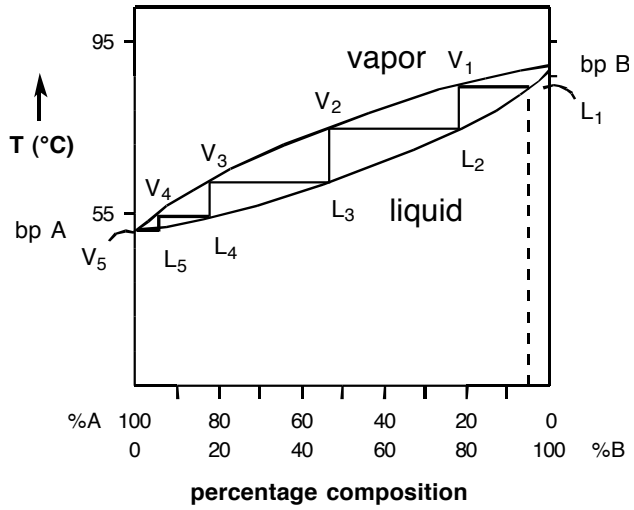


Figure 4: Phase diagram of a simple two component mixture; effect of fractional distillation.

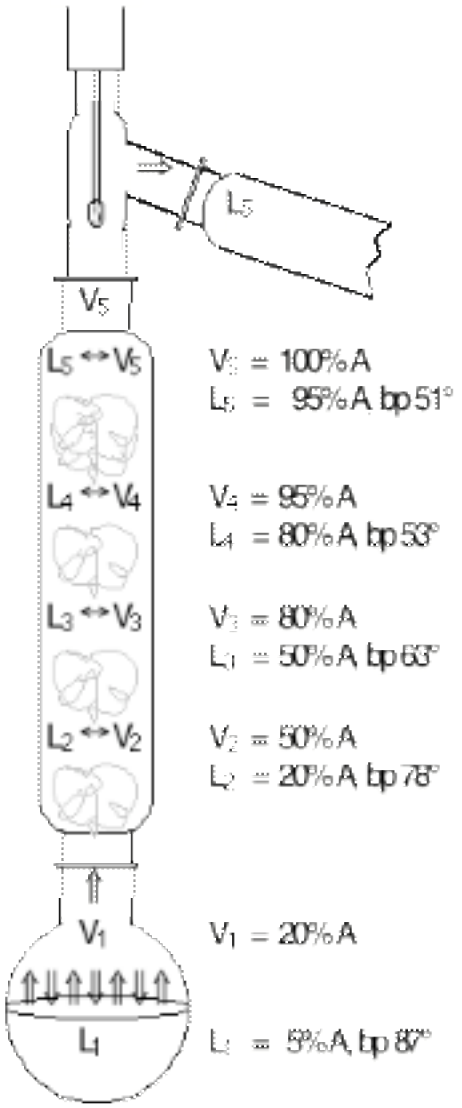


Figure 5: Fractional Distillation of a simple two component mixture of initial composition 5%A, 95%B where A is the lower boiling liquid, and B is the higher boiling liquid.

25°C. Due to this continuous enrichment of the vapor, the temperature behavior of a fractional distillation over time will resemble that shown in Figure 1C even when two components having similar boiling points are separated.

C. Gas Chromatography:

Gas chromatography (GC) is a common analytical technique used to identify volatile organic compounds. In one version of GC, a long (6 ft or more) stainless steel tube is packed with a stationary phase and placed in a temperature-controlled oven (Figure 6). An inert gas (usually helium) is passed through the column at a controlled *flow rate*, and is the mobile phase. A small amount (1μL) of a liquid sample is injected into the column and compounds are detected as they emerge from the outlet. As in other types of chromatography, the compounds exist in equilibrium

between the stationary and mobile phases: either 'stuck' on the adsorbent as a liquid or moving with the carrier gas as a vapor. Consequently, *boiling point* is the most important property for separation with GC.

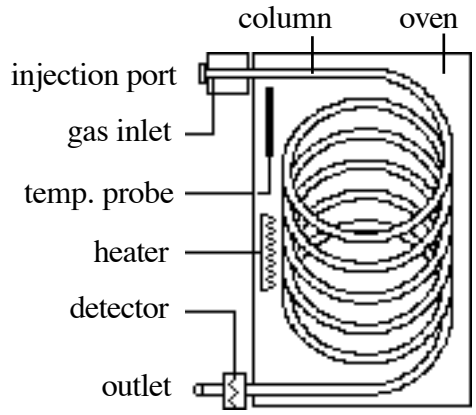


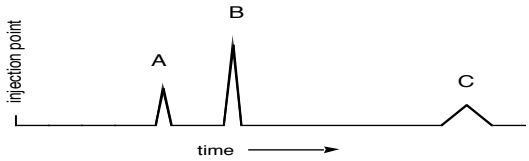
Figure 6: Schematic diagram of a gas chromatograph. To produce a chromatogram, a reference detector is required (carrier gas without sample). Consequently there are always two columns and two detectors (not shown).

However, polarity may also affect GC behavior. If two compounds have similar boiling points but very different polarities, the less polar one will come out first. Solid samples can be run on the GC by first dissolving them in an appropriate solvent. Care should be taken to inject only volatile solids.

The detector response is plotted vs. time on a chromatogram or *GC trace* (Figure 7). The time from injection to emergence from the column (a peak in the trace) is called the *retention time*, and it is analogous to R_f for TLC.

The detector response is proportional to the amount of compound passing through it, so the area under a peak is proportional to the total amount of compound in the sample. However, different compounds may produce different responses. If compounds produce the same detector response, the ratio of areas in a single chromatogram is equal to the ratio of compounds in the mixture.

In gas chromatography, the oven temperature is analogous to the polarity of the solvent in TLC: A high temperature leads to a short retention time and little separation because all compounds are vaporized and thus move at the same rate as the mobile phase. A very low temperature leads to long or nearly infinite retention times since the compounds remain adsorbed on the stationary phase. In addition, diffusion causes the peaks to spread out as the retention time increases, so compounds that are retained in the column for a long time give broad, ill-defined peaks. The injector is generally maintained at a much higher temperature than is the column to ensure that the sample is completely vaporized before it reaches the column and does not condense in the injector. The temperature of the detector is also set to prevent condensation of the sample components.



compound	bp (°C)	retention time
A	42	2.0 min
B	50	2.5 min
C	96	5.7 min

Figure 7: GC trace of a three-component mixture. Chart at right shows relative relationships between these compounds.

D. Micro Boiling Point Determination

The boiling point (bp) of a liquid is the temperature at which the vapor pressure of the liquid equals the atmospheric pressure. More practically, you see the liquid boil. The best way to determine the boiling point of a liquid is to distill it and record the temperature at which it comes

over in the distillation. However, when determining the bp of an unknown liquid (Think Experiment #9), where you have only a small amount of sample a full distillation is out of the question. So, in order to determine the boiling point of a very small sample of liquid, a technique has been developed for organic chemists to determine the boiling point of a liquid sample as small as 5-10 drops of sample.

In a Micro-scale boiling point determination, 0.5 - 1.0 mL of sample is placed in a small (75 x 150 mm) test tube that is attached to a thermometer *via* a rubber band. Then a 1.5 - 2.0 cm section of capillary is placed, **open-end down** into the sample. The whole apparatus is shown in Figure 8. The test tube/thermometer is then submerged in an oil bath. The oil bath is then warmed slowly, until the open-end of the capillary has a steady and rapid stream of bubbles emerging from it. When a rapid and steady flow of bubbles is being emitted from the capillary

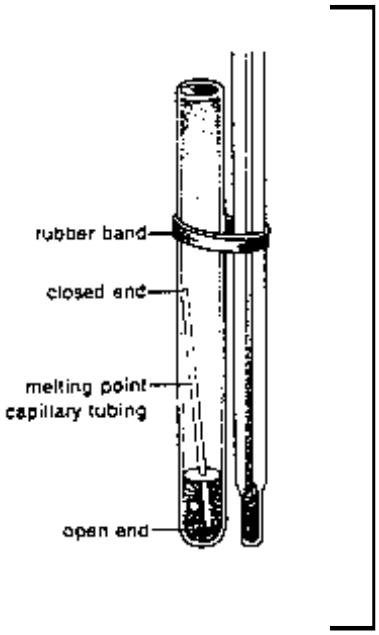


Figure 8: The micro-boiling point apparatus. Notice the capillary is positioned open-end down.

tube, the source of the heat is turned off, and the oil bath is allowed to cool at its own pace. The liquid sample will slowly cool, and when the vapor pressure of the liquid exactly equals atmospheric pressure, the bubbles will cease and liquid will be forced into the capillary tube. By definition of boiling point, this point is the boiling point of the liquid. In effect, during this experiment the liquid is heated past its boiling point (the rapid stream of bubbles from the capillary tube), and then cooled down to the boiling point slowly (when the bubbles stop and the liquid fills the capillary tube). This is done, because the cooling will almost always be done more slowly than the heating, and is therefore more accurate.

Here are some tips about micro-scale boiling point determinations. First, when you heat a sample, heat it slowly. Heating too rapidly can cause the sample to boil away before you find the melting point. Second, air bubbles trapped in the capillary tube may escape and be mistaken for the boiling of the sample. Air bubbles can be identified by the fact that they do not increase in frequency, and will often stop before they become steady and rapid. If you are unsure, stop heating the sample and see if the liquid fills the capillary tube when the sample cools. If the liquid does not fill the capillary tube, the bubbles were air and not the sample boiling. Finally, after the sample

cools, repeat the experiment by reheating the sample with the capillary tube filled with sample. This second boiling point determination is often more accurate, because the sample is in the capillary tube and air bubbles will not confuse the issue.

Procedure

You will work in pairs for the distillations. One partner will perform the simple distillation while the other will perform the fractional distillation.

A. Simple Distillation

Obtain 15 mL of a 40:60 mixture of hexanes and toluene and add it to a 25-mL round bottomed flask containing 2-3 boiling chips. Set up a simple distillation apparatus as illustrated in your text, using a 10-mL graduated cylinder in place of the receiving flask. For best results, be sure to position your thermometer such that the mercury bulb is well below the level of the adapter side arm (*cf.* Figure 4). You may also want to place a little glass wool at the bottom of the heating mantle and some aluminum foil over the flask to aid the distillation process. Remember to peek through the foil periodically so you don't distill the contents of the flask to dryness. Seal all glass joints in the apparatus with a small amount of joint grease to prevent the vapors from leaking.

Slowly heat the solution to its boiling point. Look for the separation between the organic vapors and the air above -- the condensation ring. Try to keep this ring somewhere within the elbow of the 3-way adapter, and control the temperature so the distillate collects at a rate of approximately 10 drops per minute. Do not overheat! Check regularly to see that none of the joints of the distillation apparatus is leaking. Along with overheating, this is one of the most commonly encountered problems in the experiment.

In your notebook, make a table recording the temperature and total volume of distillate collected at 0.5-mL increments. You will be collecting a total of three fractions, and for each you should also record the actual boiling point range and the total volume collected. Fraction A should include materials that distill from room temperature up to about 73-75°C. Fraction B is a transition phase and should be collected from 73-75°C to 103-105°C. The final fraction, Fraction C, should contain material collected from 103-105°C until the distillation is complete. Measure the residue remaining in the distilling flask. Store the fractions in properly labeled, sealed glass vials (wrap the lid with a small amount of Parafilm to prevent leaks), noting the names on the vials in your notebook. Determine the percent recovery for each component as indicated below.

B. Fractional Distillation

Obtain 15 mL of a 40:60 mixture of hexanes and toluene and add it to a 25-mL round-bottomed flask containing 2-3 boiling chips. Set up a fractional distillation apparatus as illustrated in your text, using a 10-mL graduated cylinder in place of the receiving flask. For best results, be sure to position your thermometer such that the mercury bulb is well below the level of the adapter side arm (*cf.* Figure 4). You may also want to place a little glass wool at the bottom of the heating mantle and some aluminum foil over the flask and over the length of the fractionating column to aid the distillation process. Wrap the column as tightly as you can with the shiny side of the aluminum foil facing inward. Remember to peek through the foil periodically so you don't distill the contents of the flask to dryness. Seal all glass joints in the apparatus with a small amount of joint grease to prevent the vapors from leaking.

Slowly heat the solution to its boiling point, and then bring the vapor up the fractionating column. Be careful not to flood the fractionating column. Again, you should try to keep the

condensation ring somewhere within the elbow of the 3-way adapter. Control the temperature to collect distillate at a rate of approximately 10 drops per minute. Be sure to check regularly to see that none of the joints of the distillation apparatus is leaking.

In your notebook make a table recording the temperature and total volume of distillate collected at 0.5-mL increments. You will be recording a total of three fractions, and for each you should also record the actual boiling point range and the total volume collected. Fraction A should include any material that distills from room temperature up to about 73-75°C. Fraction B is a transition phase and should be collected from 73-75°C to 103-105°C. The final fraction, Fraction C, should contain material collected from 103-105°C until the distillation is complete. Measure the amount of residue remaining in the distilling flask. Store the fractions in properly labeled, sealed vials (wrap the lid with a small amount of Parafilm to prevent leaks), noting the names on the vials in your notebook. Determine the percent recovery for each component as indicated below.

C. Gas Chromatography

You may analyze your samples by gas chromatography (gc) as follows: Wash a 10 μL GC syringe 5-10 times with diethyl ether (eject the ether into a waste bottle). Evaporate any remaining ether by pulling the syringe plunger in and out about 20 times. Next, flush the syringe with your sample 5 or 6 times before filling it to 1 μL. Touch the syringe needle to the wall of your sample container to remove any sample that may remain on the needle tip, invert the syringe (so that its needle points upward), and then pull the plunger out to about 3 μL. This clears your sample out of the syringe needle, and allows cleaner results in the GC analysis.

In a rapid, but controlled manner push the syringe needle through the GC septum, depress the syringe plunger all the way, and pull the needle out of the septum. Be VERY careful not to bend either the needle or the plunger. Finally, be sure to clean the syringe with diethyl ether, as before.

Analyze all fractions from the simple and fractional distillations. In each case, be sure that you can identify the peaks in your chromatogram.

D. Identification of Unknown Liquids by Gas Chromatography

In this portion of the experiment you will identify the components of an unknown liquid by gas chromatography. This will be accomplished by comparing a chromatogram of your unknown with that of a standard (known) mixture of the four unknown liquids.

Obtain a sample of one of the unknowns in your lab. This unknown will contain one compound in the standard mixture. Be sure to record your unknown number in your notebook. Analyze your sample by gas chromatography (GC) as described below. Your TA will assist you.

Wash a 10-μL GC syringe 5-10 times with diethyl ether (eject the ether into a waste bottle). Evaporate any remaining ether by pulling the syringe plunger in and out about 20 times. Next, flush the syringe with your sample 2 or 3 times before filling it to 1 μL. Touch the syringe needle to the wall of your sample container to remove any sample that may remain on the needle tip, invert the syringe (so that its needle points upward), and then pull the plunger out to about 3μL. This clears your sample out of the syringe needle, and allows cleaner results in the GC analysis.

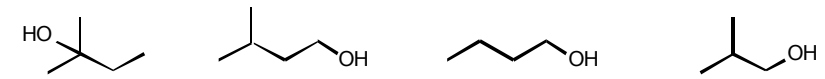
In a rapid, but controlled manner push the syringe needle through the GC septum, depress the syringe plunger all the way, and pull the needle out of the septum. Be VERY careful not to bend either the needle or the plunger. Finally, be sure to clean the syringe with diethyl ether, as before.

Obtain a gas chromatogram of the unknown and a micro boiling point for the same unknown liquid (see Part E below). Determine the identity of the peak(s) on the basis of retention time and boiling point. From the boiling point you obtained and comparison of your GC with that of the standards run by your T.A., determine which of the following compound you had: tert-amyl Alcohol, Isoamyl Alcohol, n-Butyl Alcohol, or Isobutyl Alcohol.

E. Micro Boiling Point Determination

Assemble the test tube/thermometer apparatus shown in Figure 8. Beakers filled with mineral oil will be provided for you and can be found in one of the fume hoods. The oil in your beaker should be clear enough so that you can see inside your test tube. If it is too murky, ask your TA to help you replace the oil. Make sure that your rubber band is not submerged in the oil bath (it may melt). You may perform the micro boiling point determination at your bench.

Select one of the four unknown liquids provided in the laboratory. Record the unknown number in your lab book. Place 1-1.5 mL of the sample in the test tube. Place a melting point capillary into the sample with the open-end down and the sealed-end up. Using your oil bath, heat the sample until bubbles are emitted from the capillary tube at a brisk and steady pace. Turn the heat source off and let the sample cool. Record the temperature range where the bubbles cease and the liquid fills the capillary tube. REPEAT USING THE SAME CAPILLARY TUBE. Determine the identity of your unknown sample by comparing its boiling point with the literature boiling points of the possible compounds given below:



tert-amyl alcohol b.p. 102°C | isoamyl alcohol b.p. 132°C | n-butyl alcohol b.p. 118°C | isobutyl alcohol b.p. 108°C

Calculations

Percent Recovery:

$$\text{Percent Recovery} = \frac{\text{Total Volume of Component Collected}}{\text{Volume of Component in Original Sample}} \times 100$$

Results and Discussion

Discuss your observations for both simple and fractional distillations. Draw graphs of temperature (Y axis) vs. volume collected for both cases. For each fraction, determine the actual volume of the components present, and use this information to calculate the percent recovery in each case.

Compare the two distillation techniques, discussing yield, purity, and ease of separation. Be sure to clearly explain how and why you reached these conclusions. Explain when you might use each technique.

Fill out the attached data sheet and submit it to your TA when you turn in your report. This sheet will be graded separately from your report and will not be returned. As such, you will also need to incorporate the data presented here within the body of your report.

References

Distillation

Zubrick, J.W. "The Organic Chem Lab Survival Manual: A Student's Guide to Techniques", 3rd ed. John Wiley and Sons: New York, 1992, pp 187-208; 335-336.

Harwood, L.M.; Moody, C.J. "Experimental Organic Chemistry: Principles and Practice"; Blackwell Scientific Publications: Oxford, England, 1989, pp 139-150.