Simple and Fractional Distillation

Assigned Reading:
Read Techniques 14, & 15 before you proceed. Read Technique 24 before the start of the second lab meeting.

We sill use a sand bath instead of an aluminum block for our heat source. Also, you should use a 10 mL round-bottom flask for your distilling flask (pear-shaped is alright also). In addition, use your spin vane to prevent bumping (in lieu of a boiling stone). **Note: Pay careful attention to not allowing your spin vane to be poured into the organic waste container. Your instructor will show you how to retrieve your spin vane properly from your flask.**

Pre-Lab Planning
After reading this handout and the assigned reading mentioned above, prepare your notebook so as to include a Title, Introduction, Haz-Mat, Apparatus (simple & fractional set-ups--see lecture notes), and Procedure in your notebook.

Introduction:
In this exercise you will distill a 50/50 mixture (by volume) of cyclohexane and toluene using two different methods: simple distillation and fractional distillation (Techniques 14 & 15). The composition of the distillate & residue (determined by refractometry- Technique 24) obtained will allow you to compare the efficiency of the distillation techniques. During distillation, you should carefully monitor the distillation temperature and volume of distillate. The distillation temperature is measured only when drops of condensate are actually observed forming in the well of the Hickman head. The thermometer does not measure the temperature at which the liquid boils in the boiling flask. You may expect the liquid to boil long before the vapors can make it to the well of the Hickman head.

Procedure
You should use the small, 0 to 300°C thermometer provided for this experiment which fits easily into the Hickman head without a clamp. CAUTION!!! When assembling the apparatus be absolutely sure that your internal thermometer slides easily into the apparatus. If you are unsure, check with your instructor. Furthermore, be sure all glassware, all glassware connectors, the stainless steel sponge and your pipette are absolutely clean. Use cyclohexane or toluene to condition if necessary.

The mixture to be distilled should be about 50/50 by volume and is prepared by adding 4.xx mL of cyclohexane and 4.xx mL of toluene together in a clean and dry 10 mL graduated cylinder (4.xx means approximately 4 mL measured precisely to the nearest 0.01 mL). The mixture should be mixed well and stored in a corked flask until needed (why should you NOT use a rubber stopper?). Subsequent volume measurements of the volumes of distillates or residue can be made with a serological pipet or graduated cylinder as needed. However, be sure these volume-measuring devices are clean and dry so as not to contaminate the liquids whose volumes are measured and be sure to note which devices you used in this, and in all future experiments.

All volumes of distillates are to be transferred to, and kept in tightly-corked and clearly labeled small test tubes for subsequent use. You will need two tubes marked SD-distillate & SD-residue for simple distillation and two tubes marked FD-distillate & FD-residue for fractional distillation. Prepare these test tubes prior to distillation!

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1 You should always record the volume-measuring device used.
Part I: Simple Distillation

Assemble a simple distillation setup similar to the one shown below (Note: we will not be using a thermometer to measure the temperature of the sand bath). Use a 10 mL round-bottom flask containing your spin vane. You will use a sand bath in a 150 mL beaker. Note that this entire apparatus must be an open system. Also, all connecting adapters joining glassware must be tight so as to avoid loss of distillate. The purpose of the spin-vane is to prevent bumping and provide even heating of the volume of liquid to be distilled. You may have to use aluminum foil to help monitor the temperature around the sand bath.

Add 3.xx mL of your cyclohexane / toluene mixture to the round-bottom flask (about 3.3x mL is preferred). Before you start to heat, be sure that you spin vane is actually stirring. You may have to lower your apparatus deeper into the sand bath so that the spin vane is closer to the magnetic spin mechanism in the hot plate. Heat the mixture in a sand bath sitting atop your hotplate. Heat to boiling and lower or raise the power setting so that you distill the mixture at an acceptable rate (see Pavia). A successful distillation requires a very slow distillation rate. Watch for a reflux ring and observe the rate at which drops are formed on the tip of the thermometer and returned to distillation flask. Closely follow the advice regarding rate of heating found on page 712 of Pavia! If you find that you are distilling the mixture much faster than this or if the mixture should bump, return the distillate to the distilling flask and start over. While it is necessary to distill slowly to achieve best results, you should also strive to distill at a steady rate. You need to place an aluminum-foil "tent" around your distillation flask in order maintain a steady temperature. If you do this, you will find the rate of distillation may be controlled by opening or closing the tent slightly. But if you see that the distillation rate is slowing down or stopping even with the tent entirely closed, increase the transformer setting. Note that there is quite a time lag between a transformer adjustment and the desired temperature change.

Record the distillation temperature when the first drop of distillate is collected and then note any change in temperature as the well fills and / or with the passage of time. Empty the well from time to time by opening the cap on the Hickman side arm, inserting your pipet, and transferring the distillate to the tube labeled SD-distillate (be sure to re-cork the test tube). Record the temperature each time the well is emptied with your pipet. Stop distillation when about half the volume of mixture had distilled OR if the distillation temperature rises above 95°C, whichever comes first. Quickly, as soon as you stop the distillation, raise the apparatus out of the hot sand bath and remove and cap/cork the still hot distillation flask (Caution! The glassware and sand-bath are hot!) Measure or calculate the total volume of SD-distillate and measure the volume of the cooled residue, SD-residue, using either your serological pipet or your graduated cylinder (note method in observations). The difference between the 3.xx mL of mixture you started with & the sum of collected distillate and pot residue is the assumed holdup for the distillation apparatus. Calculate and report this value.
Part II: Fractional Distillation

Assemble a fractional distillation setup similar to the one shown below (Note: we will not be using a thermometer to measure the temperature of the sand bath). Use a 10 mL round-bottom flask containing your spin-vane. The fractionating column is simply a water condenser that is loosely packed with clean stainless steel sponge. All glassware, connecting adapters, and stainless-steel sponge must be clean and dry. This condenser must be dry & your entire apparatus must be an open system; all connecting adapters joining glassware must be tight. To prevent excessive heat loss, you will need a loose tent of aluminum foil around the water condenser starting just below the well of the Hickman head and extending down to the round-bottom flask. Position the tent so that you may open and close it easily for inspection. Be sure that all the adapters that join the separate pieces are tight and that the apparatus does not sag or bend.

Place a spin-vane or stirring bar in the flask and add 3.00 mL of your cyclohexane / toluene mixture. Proceed with the distillation as before. One major exception will be that a higher power setting will be required before the first drop of distillate will appear. (Initially, I suggest a 25% higher power output than was required for simple distillation; but once the vapor reaches the thermometer bulb, reduce the heat and then distill at a slow rate.) You will get a sense of how much power input is required by watching the condensation ring rise slowly up the reflux column. If at first you cannot see this ring, you can locate it by touching the reflux column with your fingers since there is a large temperature difference of the column just above and below the ring. If the heat input has been very carefully adjusted, the distillation will cease and the temperature will begin to drop just as the last of the
cyclohexane is distilled. Try not to allow the temp of the fractionating column to drop significantly: As before, record the distillation temperature and measure the volumes of distillate removed from the well of the Hickman head and transferred to the test tube marked FD-distillate. Stop the distillation when you have about half of the volume of the original mixture has distilled or when there is a significant (>10°) and somewhat sudden drop off in observed temperature, whichever comes first.

Carefully raise the apparatus and remove and cap or cork the hot distillation flask. Measure or calculate the total volume in FD-distillate and, when the distillation flask has cooled, measure the volume of pot residue. Transfer it to the test tube marked FD-residue and determine the holdup volume as before. All volumes should be stored in tightly corked test tubes covered with a SMALL square of Parafilm.

Part III: Analysis of distillates and Residues Using Refractometry

The composition of the distillates can now be determined using refractometry (Technique 24). After you have read Technique 24, studied the online slide show (on our class website), and the instructor has demonstrated the use of this expensive instrument, determine the refractive indices of SD-dis. SD-res, FD-dis, and FD-res at ambient temperature (use the thermometer that is mounted on the refractometer)\(^2\).

Caution! Be sure that you use only plastic transfer pipettes to apply liquid to the refractometer prism. Also, be sure that you only blot (not wipe!) the prism with a soft tissue.

Since the ambient temperature at which you measured the refractive indices of your distillates & residues is not precisely 20°, you will need to correct the refractive indices to 20°C. The following formula works well for temperatures close to twenty degrees.

\[
 n_D^{20°(corrected)} = n_D^{\text{ambient}} + (t^{\text{ambient}} - 20)(0.00045)
\]

Look up the refractive indices of pure toluene and of pure cyclohexane in either Lange's or the CRC (cite reference). Since the refractive index of a binary mixture is a linear function of the mole fraction, you may calculate the % of cyclohexane and of toluene in each fraction and residue using the following formula:

\[
 X^B = \frac{(n_D^{20°(corrected)} - n^A)}{(n^B - n^A)} \quad \text{Note! All n’s corrected to same temp.}
\]

Where \(X^B\) is the mole fraction of component B in a binary mixture of A & B; \(n^A\) and \(n^B\) are the refractive indices of pure liquid A and pure liquid B; \(n_{\text{sample}}\) is the refractive index of the liquid sample (SD1, FD1, SD-residue, etc.) mixture of A & B. All refractive indices are at 20°C. Use this formula in your notebook but do not use A & B for symbols. Instead use cyc and tol for cyclohexane and toluene.

Be sure that you include in your notebook clearly labeled calculation section that contains: a) mole-% of cyclohexane and toluene in original mixture (based on volumes used & literature values of densities), b) corrections of measured refractive indices at ambient temperature to 20°C, and c) calculations of mole-% of cyclohexane and toluene in the various fractions (based on refractive indices). Observe that for a binary mixture, \(X^B + X^A = 1\). For clarity, you must express the formula used in the calculation, identify the symbols in the formula, and then substitute numerical quantities (see note on your laboratory notebook).

Save all fractions for further analysis by gas chromatography in Lab 08. Place a cork on the samples and Parafilm the tops to minimize loss of liquid via evaporation.

\(^2\) All of these mixtures should be clear and colorless. If any mixture is cloudy or colored, it is due to contamination and you should skip the determination of the samples refractive index.
Prepare a table in your notebook with the following information in your calculations section:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volume (mL)</th>
<th>Measured $n_D^{ambient}$</th>
<th>Corrected to $n_D^{20}$</th>
<th>mole% C$<em>6$H$</em>{12}$</th>
<th>mole% C$_7$H$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SD-Residue</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Holdup</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FD-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fd-Residue</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Holdup</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

From your table, you should be able to draw some conclusions regarding the purity of the different fractions you collected by simple and fractional distillation methods. Compare the purity of the fractions obtained for the two methods. Also compare the holdup for the two methods.

In addition, you should include the following table in your conclusions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>mole% C$<em>6$H$</em>{12}$</th>
<th>mole% C$_7$H$_8$</th>
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<tbody>
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<td>Fd-Residue</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Postlab Questions:**

Answer the following questions in your lab notebook after your conclusions.

1. What is a minimum BP azeotrope? What causes this?
2. What is a maximum BP azeotrope? What causes this?
3. What will distill first? Toluene or cyclohexane? Why?
4. Use vapor-temperature diagrams to explain the difference between simple and fractional distillation.
5. Why is the column in fractional distillation packed with steel mesh?