Part A: Fractional Distillation of Alkanes


**Introduction:**

The objectives of this experiment are to separate a mixture of two hydrocarbons by fractional distillation and evaluate the efficiency of the separations. Distillation has been used since antiquity to separate the components of mixtures. In one form or another, distillation is used in the manufacture of myriad perfumes, flavor ingredients, liquors, and a variety of other organic chemicals. One of its most important modern applications is in refining crude petroleum into fuels, lubricants, and other petrochemicals. The first step in the refining process is separation of crude petroleum into various hydrocarbon fractions by distillation through huge fractionating columns, called distillation towers, that are hundreds of feet high. Since components of different molecular weights and structures usually have significantly different boiling points, this process separates the petroleum into portions containing hydrocarbons of similar carbon content and properties.

**Overview and some theory**

Fractional distillation is a simple technique for accomplishing a large number of simple distillation/separations, in a single continuous operation. A fractionation column (fractional distillation column) has an extensive surface area for exchange of heat between ascending vapor and descending liquid (condensate). As the condensate accepts heat from the vapor at any point in the column, the condensate is partially vaporized and the vapor is enriched in the more volatile component. At the same time, as the vapor loses heat to the condensate, a part of the vapor condenses and the condensate becomes enriched in the less volatile component. Eventually, the vapor that condenses at the top of the column is pure or enriched in the more volatile more pure. Similarly, the condensate that has returned to the distillation flask is pure or enriched in the less volatile component.

The ability to separate two liquids depends on the differences in the boiling points of the two liquids as well as a number of other factors, some being the rate of the distillation, insulation of the column and on how efficient the column is. In order to achieve good separation, an even heating is required along with low rate of distillation to maintain as much as possible a thermal equilibrium and a high reflux ratio. Furthermore, the type of column, the column packing and the process of packing a column all determine the efficiency or ability that a column has for separating the components of a liquid mixture.

In this experiment you will separate a mixture of hydrocarbons by fractional distillation and monitor the progress of the process by collecting several fractions that distill at different temperatures. Then you will determine the composition of these fractions (the ratio between the two components) using a gas chromatograph (GC). Gas chromatography is an analytical method that is used for qualitative (chemical identity) and quantitative analysis of volatile compounds. Once the composition of the fractions is known, you will be able to evaluate the quality of your separation. This is done by plotting the amounts of the two alkanes in each fraction (mole fraction) versus the average boiling point of the fraction. You will also determine the efficiency of your fractionating column by calculating the number of theoretical plates, \( n \), and the height of the column equivalent to one theoretical plate, the HETP. The higher the \( n \) — and thus the smaller the HETP — the more efficient the column. The number of theoretical plates in your distillation apparatus can be calculated from the Fenske equation:

\[
\log(Z_A/X_A) - \log(Z_B/X_B) = \frac{\log \alpha}{\log \alpha}
\]

(1)

\( X_A \) and \( X_B \) represent the mole fractions of the two alkanes (A and B) in the liquid, and \( Z_A \) and \( Z_B \) are the corresponding values for the vapor exiting the column and condensing. \( \alpha \) is the volatility factor that can be estimated from the boiling points (\( T_{bA} \), *in degrees K*) of the two alkanes by equation 2.

\[
\log \alpha = 8.9 \frac{(T_{bB} - T_{bA})}{(T_{bB} + T_{bA})}
\]

(2)

When using this equation, keep in mind that the boiling flask counts as one theoretical plate, so the number of plates provided by the column will be \( n - 1 \).
The theoretical plate calculation can be done at any point during the distillation — all you need to know are the mole fractions of the two compounds in the liquid and the vapor. Of course this can be done at any point through the distillation, but it's not easy to find out the composition of the solution in the boiling flask. Therefore the best time to make the measurement is right at the beginning, since you know exactly how much of each compound you put in the flask. So, to determine \( n \), what we need is the composition of the liquid initially in the boiling flask and the composition of the vapor that first emerges from the top of the column and condenses into a receiving vial. We'll call this the "HETP sample".

**Fractional distillation**

You will be assigned two hydrocarbons from the list below. You will measure out the equal volumes of each and combine them. *Be absolutely certain that you take the ones you were assigned (A student who can't select the right chemical is an accident waiting to happen!)*

**Possible components of mixture**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( bp ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )-hexane</td>
<td>69</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>81</td>
</tr>
<tr>
<td>( n )-heptane</td>
<td>98</td>
</tr>
<tr>
<td>isooctane (2,2,4-trimethylpentane)</td>
<td>99</td>
</tr>
<tr>
<td>methylcyclohexane</td>
<td>100</td>
</tr>
<tr>
<td>( n )-octane</td>
<td>126</td>
</tr>
</tbody>
</table>

All the hydrocarbons are very flammable and may irritate the skin, eyes, and respiratory tract. Minimize your contact with the liquid and its vapors, and keep the compounds away from hot surfaces and open flames.

**Caution: make sure that you never heat a liquid at atmospheric pressure in a closed (unvented) system.** There are better ways to prove that \( PV=nRT \)! If you're lucky the resulting increase in pressure will blow a joint apart, otherwise you and your neighbors could end up full of glass shards. This shouldn't be a problem if you've set up the apparatus correctly.

**Assembly of fractional distillation**

Pack a fractional distillation column with the copper mesh provided. *Your TA will demo this procedure for the class.* Be careful not to break the fragile glass fingers at the bottom of the distillation column when positioning or inserting the copper mesh. Assemble a fractional distillation system as described in figure 4.1. Clamped the parts onto a stand (not shown in the figure).

**Figure 4.1**

Assembly of Fractional distillation systems.
As the heat source you will use a heating mantle controlled by a variable transformer (or "variac") — **important: never plug a heating mantle directly into the wall outlet — plug it into a variac only!** The heating mantle should be placed on a jack and not directly on the bench. This allows lowering the heating mantle away from the flask if you need to cool it down fast.

Connect the system to cooling water. Note that the water flows through the condenser "uphill", i.e., from the receiver end toward the thermometer end. Always use the amber latex tubing for water (you can also use the clear Tygon (PVC) tubing, but not the heavy-walled black pressure tubing), and make sure it's on tightly. You don't need water gushing through it — just enough flow to keep the condensers cool.

Get 5 clean, dry vials with a capacity of about 10 ml and tight-fitting caps. You will use these to store the fractions that you collect and the liquid that remains at the end of the distillation. Have a few small flasks ready as well. Also get a small clean, dry vial with a tight-sealing cap to collect and store the HETP sample. These vials will be available in the lab.

**Distillation**

Measure out 15 ml of each hydrocarbon and pour them both into a 50-ml round-bottom flask. Add a boiling chip or two and connect the flask to your distillation setup. Make sure that the thermometer is positioned correctly. Begin heating the mixture. Watch the vapors rise in the column as you heat the boiling flask. When the vapors reach the still head, try to reduce the heating rate just enough to keep the ring of condensing vapors between the top of the column packing and the opening to the condenser for several minutes. This will give the vapor composition a chance to stabilize before any distillate is collected. If there is any water present, the first few drops of distillate will be cloudy and should be discarded (into the waste container). Collect the first half ml (approx) of distillate in your small vial and cap it tightly. This is your "HETP" sample. Record the temperature and replace this vial with a large one. Collect 5 fractions of about 5 ml each, and record the temperature range at which each one distills (the temperature when you begin and end collecting each fraction). There should still be about 5 ml of liquid left in the distillation flask — **be sure to stop before the distillation flask goes dry!**

"Distilling to dryness" is probably not a serious hazard in this experiment but can often cause major problems; depending on what "gunk" might be left in the pot and how hot it gets. Stop the distillation and allow the flask to cool. Transfer the remaining liquid to a vial and cap it tightly — you're going to analyze this one.

To prevent the HETP sample from evaporating before you have a chance to analyze it, wrap the cap with parafilm, put in inside another tightly capped vial, and give it to your TA to store in the refrigerator. This vial MUST be properly labelled! Any samples you keep in your drawer need only be labeled with the contents (compound names) and fraction number or letter or whatever you're using to keep track of what's what.

The quality of your separation will depend mainly on the distillation rate and the column efficiency. A good separation requires even heating and a low rate of distillation to maintain a high reflux ratio, so patience will be required to get good results. The efficiency of the column is a function of its length, the type of packing, and the care with which it was packed. To maintain a high reflux ratio it's best not to insulate the column (unless you're working in a very drafty part of the lab — like a fume hood... hint: don't do this in a fume hood).

The GC analysis will be conducted during the following lab periods or during the dry lab. Sign-up sheets will be posted for each section. Instructions for GC analysis will be posted separately and are not required for the prelab writing.

Once you obtained you GC results calculate the mole fraction of each component in every fraction. Plot a graph of the average boiling temperature vs. mole fraction for each component.

Calculate the number of theoretical plates.

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**Things to think about before lab —**

i. What is the "reflux ratio"?

ii. At the last minute, your neighbor (not you!) decides to wash his packed fractionating column with water so it's squeaky clean for his distillation. For some reason all his fractions are cloudy and there are tiny droplets all over the inside of his apparatus. What's wrong?

iii. Why does the water go in the bottom of the condenser and out the top instead of the other way?

iv. Explain, in conceptual terms, how a 50:50 mixture of two compounds can have a boiling point higher than that of the lowest boiling component.

v. Does the thermometer in the still head measure the boiling point of the liquid in the boiling flask or the distillate? Are you sure?
vi. Note carefully the position of the thermometer in diagrams 4.1. As you will see, the vapor coming off the column will take a fairly direct route to the condenser. That is, the vapor normally will not hang around in the upper part of the still head. With that in mind, how would placing the thermometer about an inch too high affect the temperature reading?

vii. Suppose your neighbor's distillate (not yours!) starts coming over about 15 °C below the bp of her lowest boiling component. Is this to be expected? If not, suggest at least two errors that might be responsible.

Also consider/work the following situations/problems.

1. Use the P-T nomograph on p 148 to answer the following questions.
   (a) What pressure would be required to get nicotine (bp = 247 °C) to boil at room temp (25 °C)?
   (b) At what temperature would nicotine boil at a pressure of 80 torr?
   (c) What is n-decane's approximate boiling point at a pressure of 0.01 torr?

2. You want to cook some eggs in your kitchen.
   (a) As you begin to heat the water, but well below the boiling point, you see small bubbles forming. Why? (Hint: What might be dissolved in water that would start to come out as a gas as the temperature is raised?)
   (b) As the liquid boils, lots of large bubbles form and rise to the surface. A person with only a minimal knowledge of chemistry might claim that these bubbles contain hydrogen and oxygen, or that they contain air. How would you briefly explain what's really going on and why such a proposal makes no sense?
   (c) It takes longer to boil eggs (i.e., cook them in boiling water) in Denver (elevation ≈ 1 mile) than it does in San Diego. Why?

3. Use plot Graph I below to answer the following questions for a Toluene/Hexane mixture.
   (a) What is the boiling point of a mixture of 10% (by mol) hexane and 80% toluene?
   (b) What is the composition of the vapor that would distill from such a mixture?
   (c) What is the boiling point of the distillate?
   (d) What happens to the composition of the original mixture as the distillation proceeds?
   (e) Approximately how many distillation steps (theoretical plates) would be required to get an initial distillate that is about 95% hexane and 5% toluene?

4. Use plot Graph II below to answer the following questions for an ethanol/water mixture.
   (a) What is the boiling point of a mixture of 15 ml of EtOH and 30 ml of H₂O? (Careful those aren't mol fractions!)
   (b) Suppose you did a fractional distillation of a mixture of 99% EtOH and 1% H₂O using a column with about 150 theoretical plates. Briefly describe how the composition of the distillate would change throughout the distillation (beginning to end).
Isolation of Eugenol from cloves: An exercise in isolating a natural product

Overview

In the next lab you will perform an exercise in isolating a natural product from a plant. The generic term ‘natural product’ refers to any compound that is produced by plants or animals. Isolating organic compounds from natural sources is of major importance for the chemical industry. These compounds are used either in their native form or they serve as starting materials for further chemical modifications. Isolating a natural product requires developing of a purification scheme. We will demonstrate this by isolating eugenol, the compound responsible for the characteristic aroma of cloves.

Essential oils

Essential oil is a common name for fragrant volatile compounds extracted from plants. Common essential oils are citrus oil, rose extracts, mint and eucalyptus. Essential oils are found in more then 2000 plant species and they are present in various parts of the plants. They are produced by the plants and serve a wide spectrum of biological functions such as protection against natural parasites and predators, attraction of pollinates and inhibition of germination. Humans have discovered the essential oils early in history. Parts of plants that contain essential oils were used for flavoring food and drinks, as perfumes and as medicinal remedies.

Today essential oils are usually isolated from the plants and are used in their purified form in the food and perfumery industries. In addition, essential oils have pharmacological use mainly as antiseptics. Essential oils show antibiotic activity against a wide spectrum of bacteria. Some essential oils have minor local anesthetic effect and can produce an increase in blood circulation. These compounds are used in ointments for relieving sprains and muscular pain. Many other pharmacological properties are attributed to essential oils in traditional and alternative medicine.

Isolation of essential oils by steam distillation

Steam distillation is a separation technique that takes advantage of the fact that a mixture of immiscible liquids will boil at a lower temperature then the boiling temperature of the individual components.

Assume that we have a mixture of two immiscible liquids A and B. To make the case easier, let’s assume that one liquid is water and the other liquid has a higher boiling point (150°C).

Because the liquids do not interact with each other the total vapor pressure above the solution is equal to the sum of the individual vapor pressures of the pure liquids:

\[ P_{\text{total}} = P_A^\circ + P_B^\circ \]

Note that the equation does not contain a variable corresponding to relative amounts of the two components. This implies that that ratio between the two components is not relevant. Now let’s think logically. We know that a solution boils once its vapor pressure is equal to the external pressure (1 atmosphere under normal conditions). If we had only water then their vapor pressure at 100°C will be equal to 1 atmosphere and the solution will boil. Since we have another liquid that contributes some vapor pressure, the total vapor pressure at a certain temperature is higher then what it is for only water. Therefore the mixture will reach boiling at a temperature that is lower then 100°C. In other words, the boiling point of the mixture will be lower then the boiling point of the component with the lowest boiling point. The practical side of this phenomenon is that it is possible to dramatically lower the boiling point of one liquid by mixing it with another immiscible liquid. Therefore, it is possible to distill a liquid compound below its normal boiling point. This is advantageous since elevated temperatures promote degradation of organic compounds and by lowering the boiling temperature it is possible to distill out a liquid without the risk of decomposition.

The most common additive is water and therefore the method is known as “steam distillation”. When the mixture is boiled, the desired compound is co-distilled with the water. At first glance it seems like this method is not useful since the distillate contains a mixture; however, since this mixture is of immiscible liquids they are easily separated using a sep funnel.

Isolation of Eugenol from cloves

Cloves are dried flower buds collected from the tree Syzygium aromaticum which is native to Indonesia. Cloves are used as a spice in many cuisines. Steam distillation of cloves yields oil which is composed of eugenol, acetyl eugenol and β-caryophyllene (figure 1). The typical spicy fragrance of cloves is mainly due to eugenol. Eugenol is an oily substance which is only slightly soluble in water and is soluble in organic solvents. It is used in perfumes and also has various applications in dentistry. Eugenol is a common ingredient in mouthwash and also serves as a dental analgesic. When eugenol is mixed with zinc oxide it forms a composite which acts as a dental cement.

\[ ^1 \text{Note that the word mixture in this context is misused since the liquids are immiscible. Actually we mean that the two liquids are stirred together to form drops.} \]
The isolation scheme of eugenol has two parts. The first step is isolation of clove oil by steam distillation. The second part is the separation of eugenol from the other components of the oil by extraction. This is possible because eugenol contains an acidic phenol which is deprotonated under basic conditions. Figure 2 presents a flowchart of the isolation process.

Figure 1. The main components of clove oil.

Figure 2. Isolation scheme of eugenol from cloves.
Experimental procedure

Steam Distillation:
Grind approximately 3 grams of whole cloves using a mortar and pestle and transfer to a 100mL round-bottom flask. The whole cloves may not necessarily be ground to a powder but they should be in sufficiently smaller pieces. Add about 40 mL DI water and 2-3 boiling stones. Assemble a simple distillation apparatus and connect the round-bottom flask. Heat the system and distill slowly; the temperature at which the distillate (water and essential oil) will distill should be just under 100°C. The distillate will appear cloudy or milky since small drops of oil are suspended in the water. Collect about 30 mL distillate in an Erlenmeyer flask or until the distillate is clear. Make sure not to completely dry the round-bottom flask.

Extraction:
Transfer the distillate into a 125mL sep funnel with 10 mL of t-butylmethylether. Separate the bottom aqueous layer from the organic layer and transfer the aqueous layer back into the sep funnel. Repeat the extraction with an additional 10 mL t-BME (also known as MTBE). Combine both organic layers in a flask. Remove approximately 1 ml of the organic layer into a test tube and dry it with a small amount of Na$_2$SO$_4$. Filter the solution through a filtering pipette into a conical vial and evaporate the solution. Label this sample “crude organic”.

Transfer the remaining organic fraction back into the sep funnel and extract it with 10mL of 3% NaOH. The hydroxide will deprotonate eugenol’s phenol group, causing it to become soluble in the aqueous layer. Organically neutral compounds acetyl Eugenol and β-caryophyllene, will not be affected by the base and will remain in the organic layer. Repeat the extraction with an additional 10 mL NaOH. Combine both aqueous layers in a flask. Acidify the basic solution with 6M HCl until the solution becomes cloudy (because the HCl reprotounated eugenol, making it neutral and therefore insoluble in water). Extract the acidic solution with 10 mL t-BME. The aqueous layer should become clear. Transfer all organic layers back into the sep funnel and wash them with 10mL saturated NaCl solution. Transfer the organic layer into an Erlenmeyer and dry it with sodium sulfate. Filter the solution into a tared 50 mL round-bottom flask labeled “eugenol.” Wash the drying agent with 1-2 mL t-BME, filter, and add the solution filtrate to the eugenol flask. Evaporate the solution until only an oily residue remains. Weigh the flask and check that a stable weight is obtained.

Record the IR of the organic crude and the purified eugenol. Compare the two spectra and note which peaks disappeared during the purification.

Calculate the percentage of eugenol isolated from whole cloves.