CHE213 INNOVATION PROJECT

Presented by :
Anshika Agrawal
Tanvi Manhas
Vibhanshu
Sahil Kumar

Separation of Azeotropic Mixtures via Entrainer-Assisted Distillation

INTRO OF THE PROBLEM

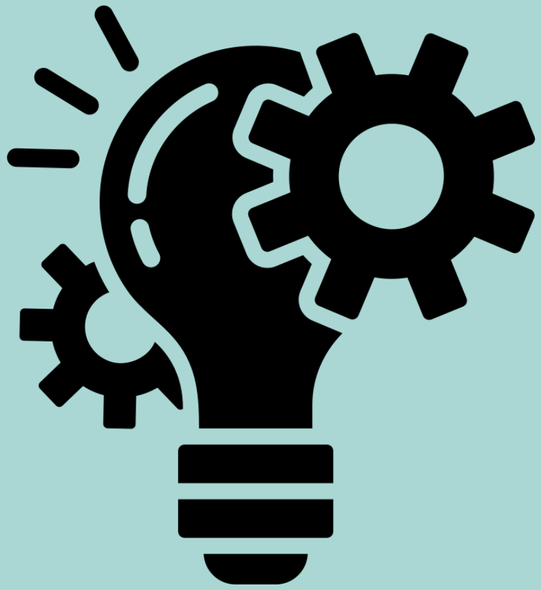
Azeotropic distillation is an advanced separation method used to overcome the limitations of simple distillation when dealing with azeotropic mixtures. An azeotrope is a specific composition of two or more substances that boil at a constant temperature, producing vapor with the same composition as the liquid mixture. This phenomenon prevents complete separation by conventional distillation.

OBJECTIVE

This experiment aims to investigate the separation of ethanol-water azeotropic mixtures using both simple distillation and azeotropic distillation. The study also explores the effect of using glycerol as a separating agent to break the azeotrope and improve ethanol recovery.

EXPERIMENTAL SETUP

- **Boiling Flask:** Contains the ethanol-water mixture; heated with a mantle or hot plate.
- **Distillation Column:** Allows vapor to rise and partially separate components based on volatility.
- **Thermometer:** Positioned at the top to monitor vapor temperature during distillation.
- **Condenser:** Cools and condenses vapor into liquid using circulating cold water.
- **Receiver Flask:** Collects the condensed distillate.
- **Glycerol Addition:** 60 mL glycerol added to 100 mL feed mixture for azeotropic distillation with entrainer.
- **Cooling System:** Provides a steady flow of cold water to the condenser.
- **Refractometer:** used to measure the refractive index of a liquid.



INNOVATION ASPECT

- The innovation in this experiment lies in the use of glycerol as a separating agent to break the ethanol-water azeotrope. Unlike conventional entrainers, glycerol is non-volatile, safe, and environmentally friendly.

- Its high boiling point alters the vapor-liquid equilibrium of the azeotropic mixture, allowing ethanol to be distilled at a higher purity than the typical 95.6% limit. This approach enhances ethanol recovery without requiring major modifications to standard distillation equipment, offering a practical, cost-effective, and sustainable method for azeotrope separation.

METHODOLOGY

Procedure:

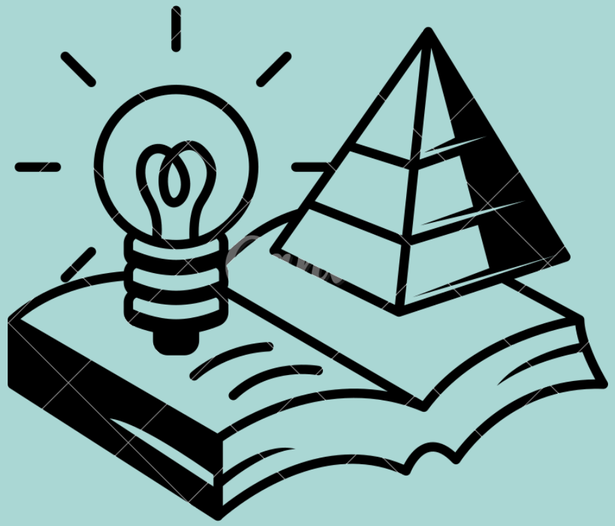
It focuses on how the distillation process is conducted, including how the mixtures are heated, how samples are taken, and how the refractive index is measured.

- Place the mixture in a boiling flask and heat it.
- Wait until the top and bottom temperatures stabilize.
- Take samples from both the top and bottom every 3 minutes.
- Use a refractometer to measure the refractive index of the samples and record the temperatures.
- Repeat for all mixture compositions.

METHODOLOGY

For azeotropic distillation without glycerol
A : 98:2 % EtOH : H2O (by volume)
B : 89.5 :10.5 % EtOH : H2O (by volume)
C : 50:50 % EtOH : H2O (by volume)
D : 25:75 % EtOH : H2O (by volume)

With glycerol (total volume - 160 ml)
A : 98 ml EtOH, 2 ml H2O, 60 ml Glycerol
B : 89.5 ml EtOH, 10.5 ml H2O, 60 ml Glycerol
C : 50 ml EtOH, 50 ml H2O, 60 ml Glycerol
D : 25 ml EtOH, 75 ml H2O, 60 ml Glycerol



THEORY

Azeotropic distillation is a specialized method used to separate liquid mixtures that form azeotropes—compositions that boil at a constant temperature and behave like a single substance during boiling. In the case of ethanol and water, they form a minimum-boiling azeotrope at around 95.6% ethanol by volume. At this point, both the vapor and liquid have the same composition, making it impossible to separate them further using regular distillation.

Without Glycerol:

- When an ethanol-water mixture near the azeotropic point is distilled, no further purification beyond 95.6% ethanol is possible because the vapor and liquid remain identical in composition. This is the limitation of simple azeotropic distillation.

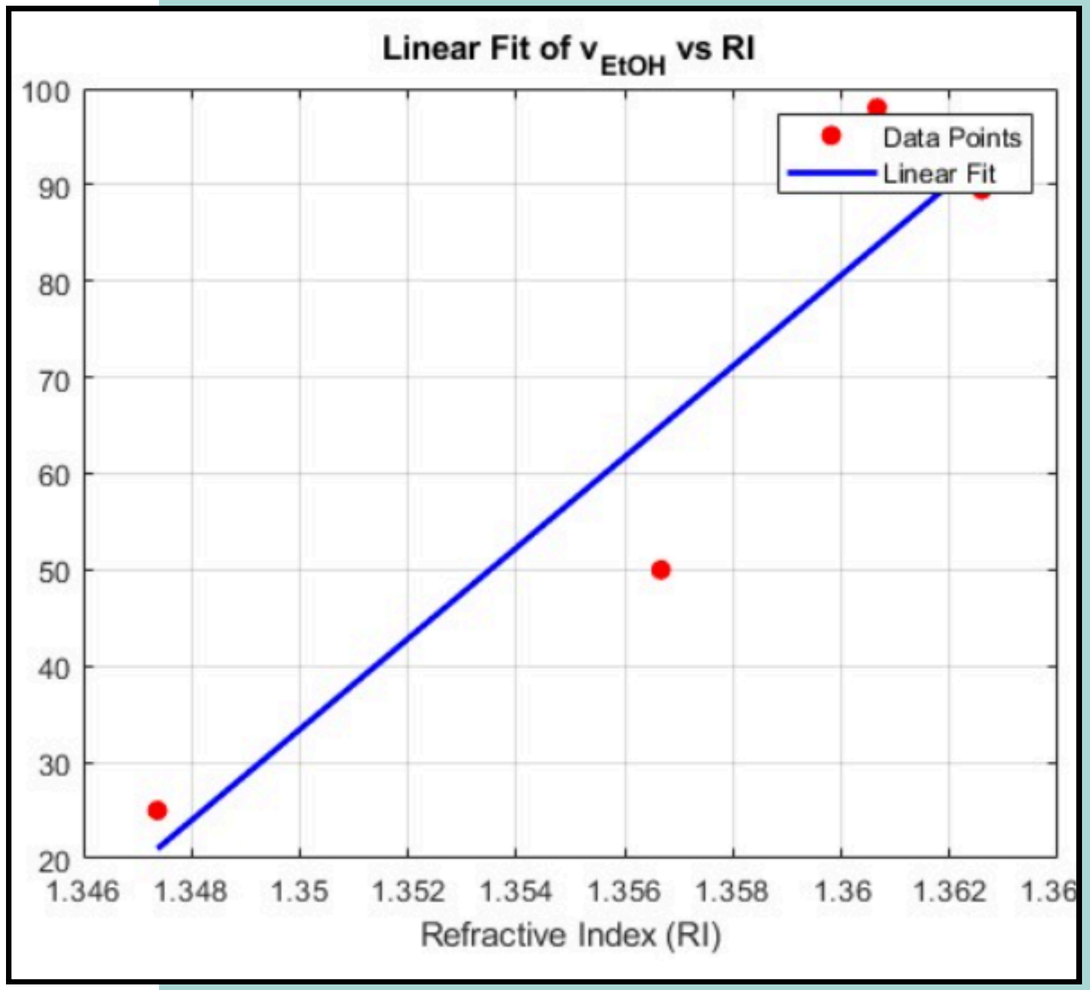
With Glycerol (Entrainer):

- To break this azeotrope, glycerol—a high-boiling, polar liquid—is added. Glycerol interacts more strongly with water than with ethanol, effectively reducing the water's tendency to evaporate. This change shifts the vapor-liquid equilibrium, allowing ethanol to become the more volatile component. As a result, ethanol can be distilled at a higher purity. Since glycerol has a very high boiling point (~290°C), it stays in the flask and can be reused in further distillations.

RESULTS

1: Calibration Data – Ethanol-Water Mixture

- Due to the absence of precise calibration data, we used the known feed compositions and corresponding refractive index (RI) values to generate a linear calibration curve. This approach is supported by literature, which suggests that ethanol-water mixtures exhibit a linear relationship between composition and RI. Our previous experiments with ethyl acetate and acetonitrile also followed this trend.
- The linear calibration fit is given by:

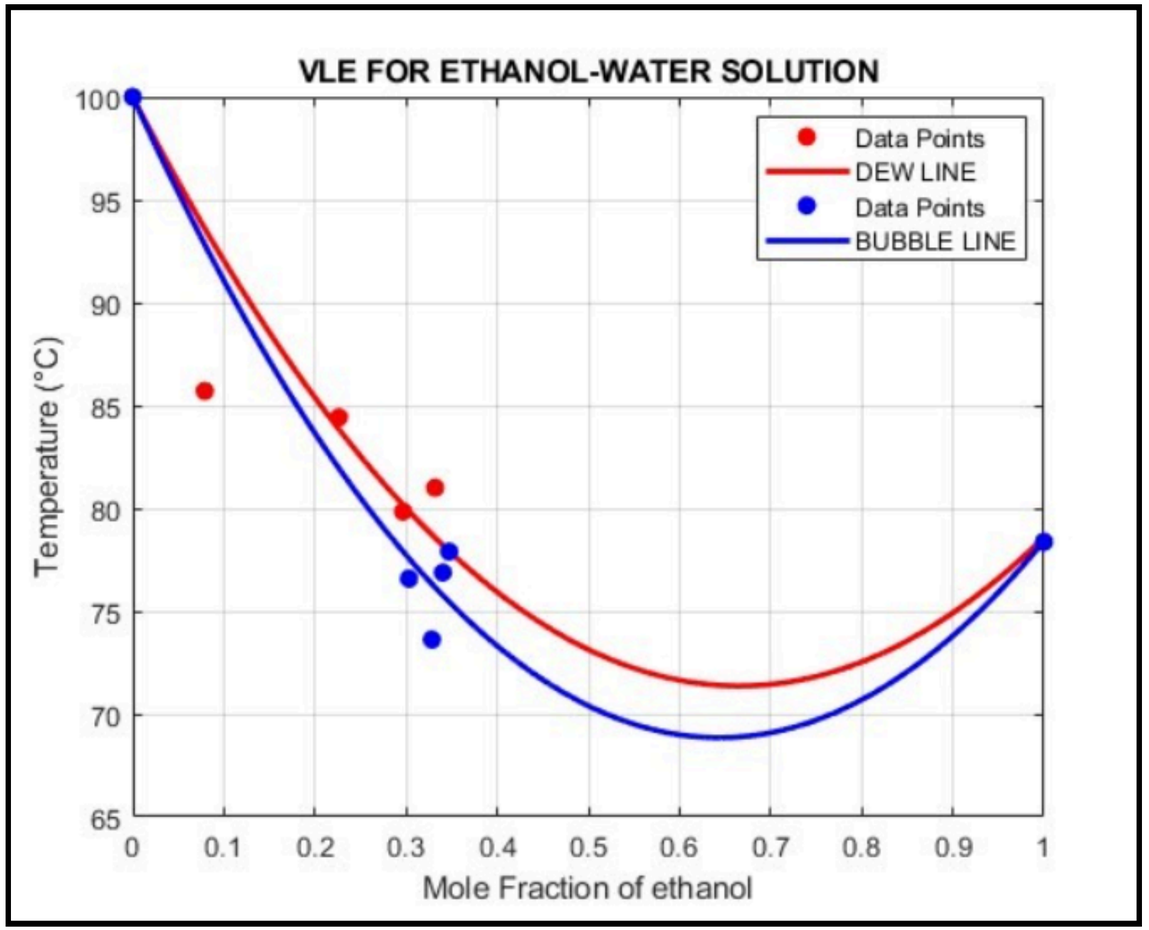


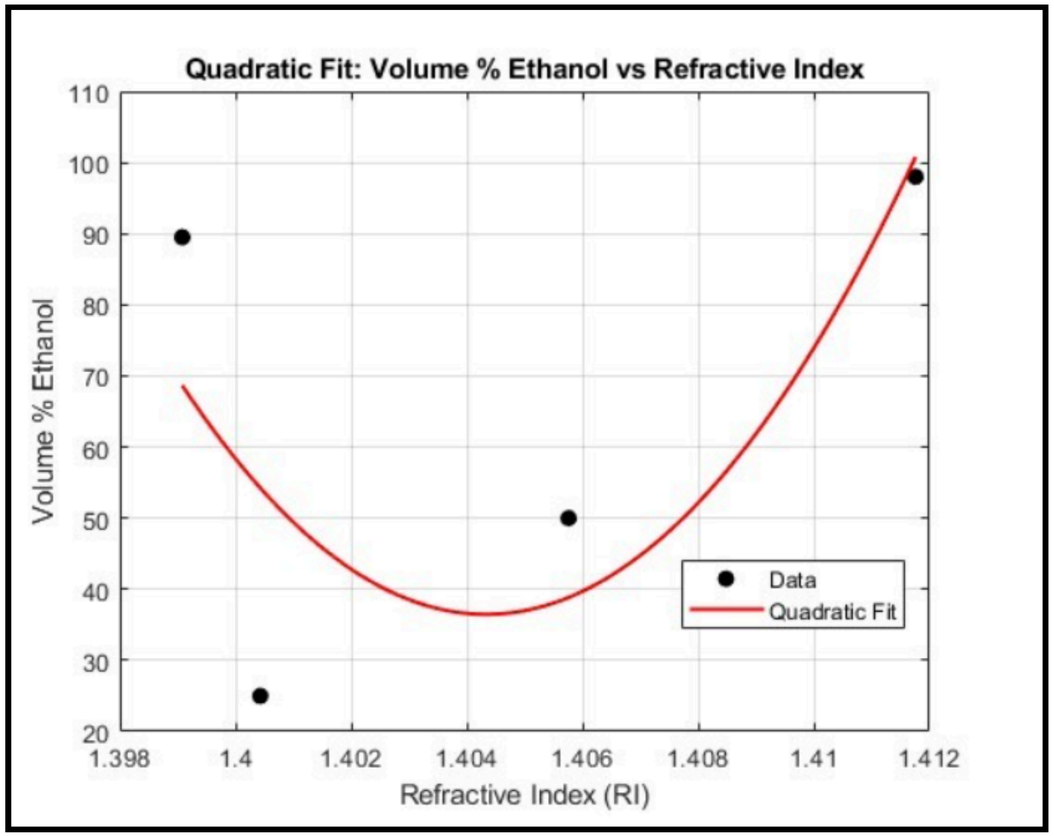
$$v\_EtOH = 4719.80 \times RI - 6338.31$$

2: T-x-y Plot for Ethanol-Water Mixture

To model the vapor-liquid equilibrium for ethanol and water, quadratic fits were applied to the temperature-composition data:

- Tx (Liquid line): $T = 64.63 \cdot x^2 - 86.04 \cdot x + 100$
- Ty (Vapor line): $T = 75.24 \cdot y^2 - 96.83 \cdot y + 100$





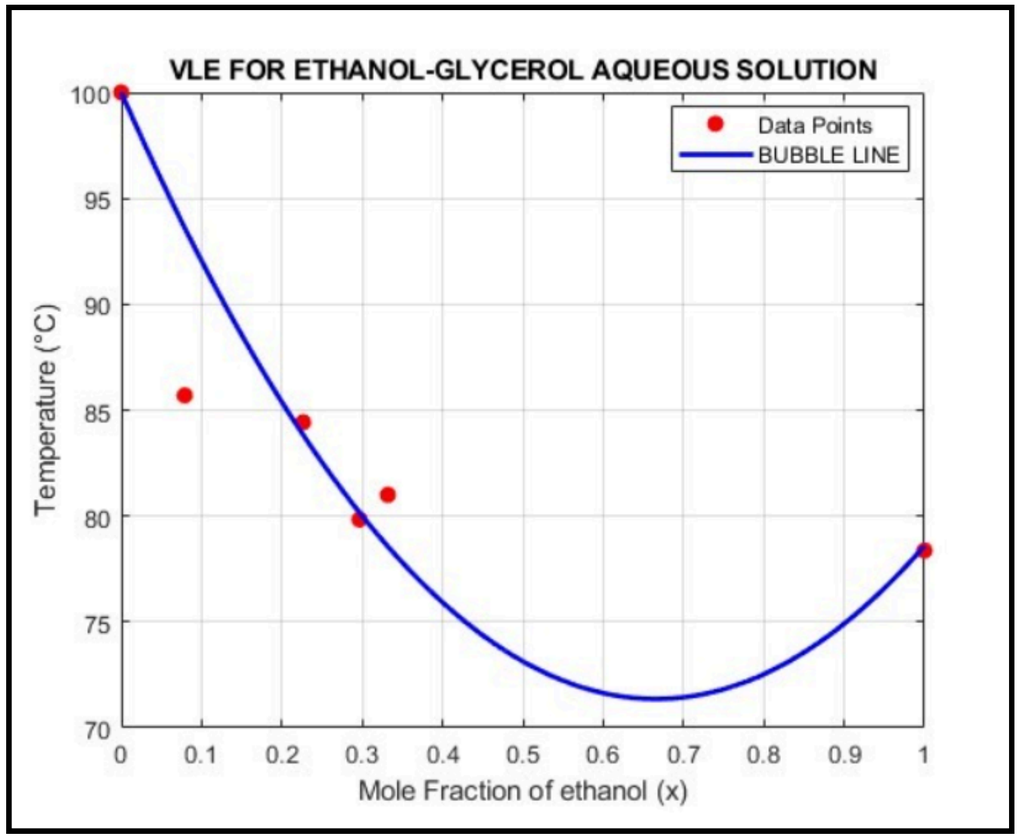
3:Calibration Data – Ethanol-Water-Glycerol mixture

Specific calibration data for ethanol-water-glycerol mixtures were not available. However, literature showed that RI-composition relationships in ternary mixtures involving glycerol tend to follow a polynomial trend. Based on this, we fit a second-degree polynomial to our measured data:

$$v = 1{,}165{,}894.36 \cdot RI^2 - 3{,}274{,}610.02 \cdot RI + 2{,}299{,}359.46$$

4: T-x-y Plot for Glycerol System

Due to limited vapor phase data for ternary mixtures, the ethanol-water azeotrope equilibrium curves were used for comparison:



Tx (Bubble line): $T = 64.63 \cdot x^2 - 86.04 \cdot x + 100$

ANALYSIS

Negative Volume Readings

Some data showed negative or inaccurate volume values. Possible causes include:

- **Calculation errors:** Indirect calculations led to incorrect derived volumes.
- **Measurement issues:** Manual volume readings may have been inconsistent or incorrect.
- **Evaporation or leaks:** Loss of vapor during distillation reduced collected volumes.
- **Incorrect baselines:** Failing to properly tare or note flask volumes resulted in faulty data.

Sources of Deviation

- **Lack of calibration curves:** Without accurate RI-to-concentration mapping, ethanol content estimation was imprecise.
- **Heating inconsistencies:** Fluctuating temperatures affected the stability of the distillation process.
- **Poor mixing:** Glycerol may not have fully mixed with the ethanol-water feed, affecting uniformity.
- **Vapor loss:** Inefficient condensation or minor leaks led to loss of volatile components.
- **Low column efficiency:** The simple lab-scale setup lacked the precision of industrial or packed columns, reducing separation effectiveness.

SAMPLE	AVG TEMP (Ty)	MOL FRACTION OF ETHANOL IN VAPOR PHASE(X)
A	77.45	-0.4852
B	77.7	-0.4851
C	78.1	-0.4860
D	78.025	-0.4862

CONCLUSION

- Glycerol addition showed some improvement in separating the ethanol-water azeotrope but did not achieve the expected ethanol purity.
- The absence of accurate calibration data (refractive index vs. ethanol concentration) limited the precision of composition analysis.
- Observed deviations indicate the need for:
  - Better process control
  - Improved calibration methods
  - A more efficient distillation setup for enhanced separation and accuracy

FUTURE WORK

- Develop an accurate calibration curve for refractive index versus ethanol mole fraction to improve composition analysis.
- Ensure thorough mixing of the feed to achieve uniform distribution of glycerol.
- Use more precise equipment for volume measurements to reduce manual errors.
- Maintain controlled and steady heating to minimize bumping and vapor losses.
- Upgrade to a fractional distillation column to enhance separation efficiency.
- Properly seal and insulate the apparatus to avoid heat and vapor losses.
- Tare and document flask volumes accurately before and after each run to ensure correct volume tracking.

THANK YOU