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Work Plan - Experiment ST5

1 Introduction

The purpose of this experiment is to gain a better understanding of the distillation principles and the parameters that affects the operation of distillation columns. It is also interesting to find the optimal operating conditions. Two tasks will be completed: Determine the time that is required to reach steady state conditions, and determine the efficiency of a column as a function of the vapor velocity. The experiment will be performed on an Oldershaw Distillation column.

2 Theory

2.1 The distillation

In a distillation process, a mixture is physically separated into two or more products that do not have the same boiling point. This happens by partial vaporization of a liquid mixture or by a parital condensation of a gas mixture. The liquid phase gets a lower volatility (with a higher boiling point) component, and the vapor phase gets a higher volatility (with a lower boiling point) component.[1]

During distillation, there are two conditions that might occur, which signalizes that the distillation is interrupted, and that the temperature of the heater must be adjusted, or turned off. The weeping point is a condition where the vapor velocity through the perforations of a tray is so low that the liquid are not able to be held out of the perforations, so instead of overflowing over the downcomer, the liquid weeps through the perforations of a sieve tray. At that point the vapor loses contact with the liquid. The flooding point is the capacity limit for the countercurrent separation. It is the result of high vapor velocity. At a high vapor velocity, the vapor pressure from below balances the gravity head of the liquid. This leads to the liquid building up in the column. The condition is reflected by the pressure drop suddenly increasing.[1]

In the distillation column there is a condenser that cools and condense the vapor that is leaving the top of the column. A total condenser will condense all the vapor from the top of the column, back into liquid. Some of the liquid sent out will be sent back to the column as reflux, and the rest is taken out as the distillate.[2]

The reflux is the portion of the vapor that is condensed and later returned to the distillation column. In this lab, the column will mostly be worked with a total reflux. That means that all vapor at the top of the column has been condensed, and is introduced back into the distillation column.

The column efficiency in a distillation column is the ratio of the total number of ideal equilibrium stages to the number of trays in the column. In an ideal distillation stage, the outgoing liquid and vapor phase establishes an equilibrium with each other. If the column efficiency is high, it indicates that there is a thorough contact between gas and liquid.

2.2 McCabe-Thiele

One of the easiest and most instructive ways to analyze binary distillations is by using the McCabe-Thiele method. It is a graphical approach presented by McCabe and Thiele in the 1920s. The method is based on the assumption about constant molar flow, that implies constant molar vapor flow rate, and constant molar liquid flow rate leaving every stage in the section. Therefore can the operating line be considered a straight line in each section of a distillation column.[1]

2.3 Gas chromatography

Gas chromatography is a separation method for separating chemical compounds to analyse them. The method uses a mobile phase, an inert gas, that is carried through a stationary phase, a liquid or a solid. The chemical compound gets dissolved in the mobile phase, that is sent through the column with the stationary phase. The separation happens because of the difference in the distributions and volatility of the gas phase compounds. The less volatile molecules will interact more with the stationary phase than the more volatile molecules, which will interact more with the mobile phase. Because of that, the more volatile molecules will pass quicker through the column than the less volatile molecules, causing the separation. A detector at the end will measure the amount of the compounds after it passes through.[3]

3 Experimental Procedure

There are two different exercises that is going to be completed; the first is: Time required until Steady State, and the second is: Efficiency vs. Vapor velocity.

3.1 Column startup

- Turn on the PC, and then the cooling water.
- Ensure that the bottom and distillate tap lines are closed.
- Fill the column with a mixture of 1730.5 mL of ethanol and 4069.5 mL of water.
- Set the column to total reflux
- Using the control box, set $T = 105\,^\circ\mathrm{C}$
- When the top temperatures changes substancially, or the pressure difference rises quickly, set the boiler's power duty to 50 %.
- Wait till the vapor stream begins to condensate: this is the "number zero" try.

The heater must be turned off immediately in the case of flooding conditions, and in the case of an emergency - turn the heater off and leave the cooling water on.

3.2 Exercise 1: Time required until Steady State

The meaning of this exercise is to calculate the time it takes to reach steady state conditions. This is the step-by-step guide on what to do on the lab:

- Set the reboiler to 50 % and wait for the column to start giving condensate.
- Within one hour, take samples from the top every fifth minute. At the end of the experiment there will be 12 top-samples.
- Take a sample from the bottom of the column after the 12th sample has been taken. The temperature and pump flow rate at this point needs to be written down.
- Analyse all the samples, and figure out how long it takes for the column to reach steady state. Steady state is considered reached when the composition of the top-samples is constant from one samlple to another one.

3.3 Exercise 2: Efficiency vs. Vapor velocity

The purpose now is to find how the column efficiency variers as a function of the vapor velocity.

- Set the reboiler at a 40% power.

- Wait till the column has reached steady-state. One can assumes that steady state is being reached in the same amount of time as in the first exercise.
- Take 20 mL-samples from both the top and the bottom. Write down the reflux rate at the time of sampling
- Set the reboiler to a new power. One should in total get 4 different velocities using 4 different boiler power settings.

3.4 Gas Chomatography

- Start with turning on the H2 supply for GC and check gas flow to GC.
- The preparation for running samples:
    - The prepared samples must be placed into the auto sampler tray, and take note of the position of the respective samples.
    - The Control Panel will be started by double clicking icon in the desktop.
    - In the Control Panel, select Launch Ethanol project. This will open Acquisition window.
    - Select Method from toolbar of Acquisition window.
    - Open the Ethanol_Quadrex_50_iso.amx method and download it to the gas chomatography.
- Running a batch of samples as sequence
    - In Acquisition window, select Sequence in the toolbar. A table appears where we will enter the sample information. (If the table does not show up; check that Table is selected under Injections. We can add more samples by clicking in table symbol.
    - Select the following:
        - Vial: Important to enter the correct position. If vial position is 1 - enter 101. If position is 2 - enter 102 and so on.
        - Sample ID: Select Sample
        - Run Type, Level, Volume, Injection source and Sample amount: These boxes will be skipped.
        - Acq. Method: Select and browse Ethanol_Quadrex_50_iso.amx
        - Proc. Method: Select and browse Ethanol_QuadrexCalibrated3.pmx
        - Sample name, Data file and Label: Type the same unique id to all three fields.
    - For each sequence provide a unique file name to have the result saved.
      YourGroupID_Data_DistilliationRigID(B01-19-8-ST4)
    - For Result Path - choose and browse folder named after Jai Kishan.
    - Run the sequence. The gas chromatography will be analyzing the samples in ascending order. Each sample will take around 7 minutes. We will see the progress of the acquisition if you select Run Queue.
- Data analysis
    - Select Run Queue and right click on our sequence. Choose Review Selected Run In Data Analysis to open Data Analysis window.
    - Click Reprocess All in the Data Analysis window toolbar.

  - Record the concentration and area of the ethanol signal and isopropanol signal area under Injection Results area.
- Turn off the H2 Gas supply.

Trondheim, January 9, 2022

Karianne Høie, Erlend Sørlie

References

[1] Heinz Preisig. Felleslab: Distillation columns. *Felleslab*, 2021.

[2] R. A. Shellie. Distillation column. `https://www.sciencedirect.com/topics/engineering/distillation-column`, 2012, Acessed 22.09.21.

[3] R. A. Shellie. Gas chromatography. `https://www.sciencedirect.com/topics/agricultural-and-biological-sciences/gas-chromatography`, 2013, Acessed 19.09.21.

[4] Wiley. *Aylward, G.H and Finlay, SI Chemical Data 7th edt.* Australia, 2014. ISBN 978-0-7303-0246-9.

[5] J. Gmehling and U. Onken. *Vapor-Liquid Equilibrum Data Collection: Aqueous-Organic Systems (Vol.1, Part 1).* Dechema, Germany, 1977.

[6] R. H. Perry and D. W. Green. *Perry's Chemical Engineers' Handbook.* McGraw-Hill, USA, 8 edition, 2008.

A Data used in the calculations

The physical properties of ethanol and water are presented in Table A.1.

Table A.1: Physical data for ethanol, EtOH, and water, H_2O.[4]

Compound	M [g mol^{-1}]	ρ [g mL^{-1}]
EtOH	46.068	0.785
H_2O	18.016	0.997

Table A.2 shows the VLE data for ethanol-water mixture at 1 atm[5]:

Table A.2: VLE data for for ethanol-water mixture at 1 atm. Collected from *Vapor-Liquid Equilibrum Data Collection: Aqueous-Organic Systems*[5].

x_{EtOH}	y_{EtOH}
0.000	0.000
0.050	0.337
0.100	0.452
0.150	0.506
0.200	0.536
0.250	0.559
0.300	0.579
0.350	0.599
0.400	0.618
0.450	0.637
0.500	0.656
0.550	0.677
0.600	0.699
0.650	0.725
0.700	0.755
0.750	0.784
0.800	0.817
0.850	0.859
0.900	0.896
0.950	0.947
1.000	1.000

B Calculations

B.1 Calculating the amount of ethanol and water in the start solution

The physical properties of ethanol and water are presented in Table A.1.

A 5800 mL mixture of ethanol and water is to be prepared. The molar composition is given as $x_{\mathrm{EtOH}} = 0.11$. This solution will be used as the start solution.

The molar amount of ethanol, n_{EtOH}, is given by

$$n_{\mathrm{EtOH}} = \frac{\rho_{\mathrm{EtOH}} V_{\mathrm{EtOH}}}{M_{\mathrm{EtOH}}} \tag{B.1.1}$$

Due to the start solution being a binary mixture, the volume of water, $V_{\mathrm{H_2O}}$, can be expressed as

$$V_{\mathrm{H_2O}} = V_{tot} - V_{\mathrm{EtOH}} \tag{B.1.2}$$

Using this, the molar amount of water, $n_{\mathrm{H_2O}}$, can be expressed using the difference between the total volume and the volume of ethanol:

$$n_{\mathrm{H_2O}} = \frac{\rho_{\mathrm{H_2O}} \left(V_{\mathrm{tot}} - V_{\mathrm{EtOH}}\right)}{M_{\mathrm{EtOH}}} \tag{B.1.3}$$

The molar fraction of ethanol in a solution is given by

$$x_{\mathrm{EtOH}} = \frac{n_{\mathrm{EtOH}}}{n_{tot}} \tag{B.1.4}$$

Combining equations (B.1.1), (B.1.3) and (B.1.4), gives the expression

$$x_{\mathrm{EtOH}} = \frac{\frac{\rho_{\mathrm{EtOH}} V_{\mathrm{EtOH}}}{M_{\mathrm{EtOH}}}}{\frac{\rho_{\mathrm{EtOH}} V_{\mathrm{EtOH}}}{M_{\mathrm{EtOH}}} + \frac{\rho_{\mathrm{H_2O}}(V_{\mathrm{tot}} - V_{\mathrm{EtOH}})}{M_{\mathrm{EtOH}}}} \tag{B.1.5}$$

The only unknown value in this equation is V_{EtOH}. Inserting all known values into the expression, and solving for V_{EtOH} gives $V_{\mathrm{EtOH}} = 1661.3\,\mathrm{mL}$. In the laboratory, a 96 vol.% solution of ethanol will be used to make the start solution. The necessary volume needed will be

$$V_{\mathrm{EtOH,96\,\%}} = \frac{V_{\mathrm{EtOH,100\,\%}}}{0.96} = 1730.5\,\mathrm{mL}$$

Using equation (B.1.2), the volume of pure water needed is calculated

$$V_{\mathrm{H_2O}} = V_{tot} - V_{\mathrm{EtOH}} = 4069.5\,\mathrm{mL}$$

B.2 Assignment

B.2.1 Distillate and bottoms composition

Firstly we need to find the volume of each pycnometer. This by using the weight of pure water (by subtracting the weight without water from the weight with water), and the known density water $\rho_{water} = 0.997\ cm^3/mL$ which gives that $V_1 = 4.992\ cm^3$ and $V_2 = 4.998\ cm^3$.

Then we calculate the density using this formula:

$$\rho = \frac{\text{weight of sample}}{\text{volume pycnometer}} \tag{B.2.1}$$

which gives the densities:

$\rho_{distillate}$=0.8229 g/cm^3 and ρ_{bottom}=0.9847 g/cm^3

From data in *Perry's Chemical Engineers' Handbook* [6] we get that the wt % of etahnol in the distillate is estimated to be 88.1, and the bottom product: 8.0 wt % ethanol. Further the mole fraction in water is given by this formula:

$$x_{\mathrm{EtOH}} = \frac{n_{\mathrm{EtOH}}}{n_{tot}} = \frac{n_{\mathrm{EtOH}}}{n_{\mathrm{EtOH}} + n_{\mathrm{H_2O}}} = \frac{\frac{m_{\mathrm{EtOH}}}{M_{\mathrm{EtOH}}}}{\frac{m_{\mathrm{EtOH}}}{M_{\mathrm{EtOH}}} + \frac{m_{\mathrm{H_2O}}}{M_{\mathrm{H_2O}}}} = \frac{\frac{wt\%_{\mathrm{EtOH}}}{M_{\mathrm{EtOH}}}}{\frac{wt\%_{\mathrm{EtOH}}}{M_{\mathrm{EtOH}}} + \frac{wt\%_{\mathrm{H_2O}}}{M_{\mathrm{H_2O}}}} \tag{B.2.2}$$

Using the weight percentage that we calculated and get:

$x_{EtOH,bottomproduct} = 0.0328$
$x_{EtOH,distillate} = 0.7433$

B.3 Vapor velocity

The vapor velocity is calculated by

$$v_{gas} = \frac{\dot{V}_{gas}}{A} \tag{B.3.1}$$

Where A is the cross sectional area of the pipe and $\dot{V}_{gas}$ is the volumetric flowrate of the gas. The cross sectional area is found using

$$A = \frac{\pi}{4} D^2 \tag{B.3.2}$$

Where D is the diameter of the column. In this experiment the column is an oldershaw column with $D = 0.07\,\mathrm{m}$, the area becomes

$$A = \frac{\pi}{4}(0.07\,\mathrm{m})^2 = 0.00385\,\mathrm{m}^2$$

The volumetric flow rate can be calculated using the ideal gas law (assuming ideal gas),

$$\dot{V}_{gas} = \frac{\dot{n}RT}{P} \tag{B.3.3}$$

Where R is the molar gas constant, T is the temperature, P is the pressure and $\dot{n}$ is the molar flow rate. Using the mass flowrate, $\dot{m}$ and the molar mass of the distillate, $M_{distillate}$, the molar flowrate can be found by

$$\dot{n} = \frac{\dot{m}}{M_{distillate}} \tag{B.3.4}$$

The molar mass of the destillate is calculated by:

$$M_{distillate} = (1 - x_{\mathrm{EtOH}})\, M_{\mathrm{H_2O}} + x_{\mathrm{EtOH}} M_{\mathrm{EtOH}} \tag{B.3.5}$$

In this case, the molar mass is

$$M_{distillate} = (1 - 0.744)\,18.016\,\mathrm{g\,mol^{-1}} + 0.744 * 46.068\,\mathrm{g\,mol^{-1}} = 38.89\,\mathrm{g\,mol^{-1}}$$

The mass flowrate of the distillate can be calculated using the reflux ratio R_{reflux} and the density of the distillate $\rho_{distillate}$,

$$\dot{m} = R_{reflux}\rho_{distillate} \tag{B.3.6}$$

In the assignment it is given that $R_{reflux} = 53\,\mathrm{mL\,min^{-1}}$, which gives,

$$\dot{m} = 53\,\mathrm{mL\,min^{-1}} * 0.8229\,\mathrm{g\,cm^{-3}} = 0.727\,\mathrm{g\,s^{-1}}$$

The molar flow of the gas can then be found using equation (B.3.4),

$$\dot{n} = \frac{0.727\,\mathrm{g\,s^{-1}}}{38.89\,\mathrm{g\,mol^{-1}}} = 0.01869\,\mathrm{mol\,s^{-1}}$$

Combining equations (B.3.1) and (B.3.3), and inserting the calculated area and molar flow, the vapor velocity is found

$$v_{gas} = \frac{\dot{n}RT}{PA} = \frac{0.01869\frac{mol}{s} * 8.314 * 10^{-5}\frac{m^3bar}{Kmol} * 298K}{1\,\mathrm{bar} * 0.00385\,\mathrm{m^2}} = 120\,\mathrm{m\,s^{-1}}$$

The gas velocity, $v_{gas} = 0.120\,\mathrm{m\,s^{-1}}$.

B.4 Number of stages using a McCabe-Thiele diagram

Figure B.4.1 shows the McCabe-Thiele diagram used to estimate the number of ideal stages for the distillation of an ethanol-water mixture. The distillate composition was given by $x_{\mathrm{EtOH}} = 0.744$ and the bottom composition was given by $x_{\mathrm{EtOH}} = 0.033$. The VLE data used to draw the equilibrium line was taken from *Vapor-Liquid Equilibrum Data Collection: Aqueous-Organic Systems.*[5] The number of ideal stages for the destillation were estimated to be 4.04.

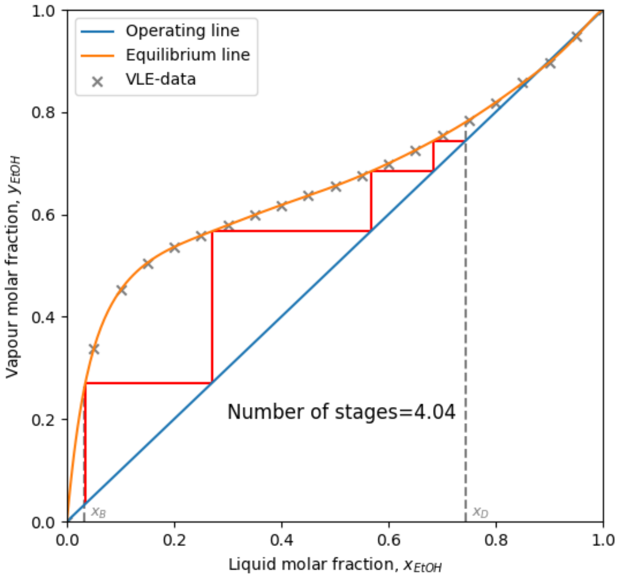

Figure B.4.1: McCabe-Thiele diagram used to estimate the number of ideal stages for the distillation in the assignment.[1]

C Health, Safety and Environment

This is not a high risk experiment, but there are always some potential risk factors involved in this experiment:

Spilling ethanol on a person or an object. Ethanol is not dangerous, so you just rinse it with water. But be careful if there is a flame close-by.

If the equipment breaks or is destroyed, it can cause a cut. In the case of cuts, it needs to be considered how severe the cut is. If it is a small cut, it needs to be cleaned and disinfected.

There is going to be some things with high temperature, and if that equipment is touched, it can cause burns. Rinse with water. Another risk about high temperature is overflow (flooding) in the column. Then the heat needs to be turned down.

Leakage from the distillation column is also a risk in this experiment. It is important to always wear personal protective gear (goggles, lab coat and gloves when required).

Considering COVID-related safety measures, it is important to wash hands when entering and exiting the laboratorium, disinfect the workspace and all of the equipment and machines that were used, and make sure to keep a distance between each other.

D Python code

Below is the python code used to plot the McCabe-Thiele diagram.

```
import numpy as np
import matplotlib.pyplot as plt
from pynverse import inversefunc

# Data given in the assignment
x_D = 0.744
x_B = 0.033


# Getting the equilibrium data, water-ethanol.
# Ethanol fractions
# The function collects the data from the datafiles.
def import_experimental_data(datafile1):
    vle_x, vle_y = np.loadtxt(datafile1, usecols=(0, 1), skiprows=1, unpack=True)
    return vle_x, vle_y


eq_x, eq_y = import_experimental_data("Datafiles/eq_data-ethanol-water.txt")


# This function plots the "stairs" in the McCabe-Thiele diagram. From top to bottom.
def draw_stairs_from_top(x_D, x_B, eq_line_inv, op_line):
    op_line_x_intercept = [x_D]
    opx = op_line_x_intercept[-1]
    opy = x_D
    while eq_line_inv(opy) >= x_B:
        eqx = eq_line_inv(opy)
        eqy = opy
        plt.hlines(eqy, eqx, opx, linestyles="-", colors="r")
        opy = op_line(eqx)
        plt.vlines(eqx, opy, eqy,
                   linestyles="-", colors="r")
        opx = eqx
        op_line_x_intercept.append(opx)

    eqx = eq_line_inv(opy)
    eqy = opy
    plt.hlines(eqy, x_B, opx, linestyles="-", colors="r")
    plt.vlines(x_B, op_line(x_B), opy,
               linestyles="-", colors="r")
    fraction_of_step = (opx - x_B) / (opx - eqx)
    n = len(op_line_x_intercept) - 1 + fraction_of_step
    return n


# Operating lines, the are the same because we have total reflux
# => R= infinity, q = 1. upper_op_line=lower_op_line=, y=x.
def op_line(x):
    return x


# Creates x-values used in plots
x_values = np.linspace(0, 1, 300)
# Find as function for the eq-line, and its inverse
f = np.poly1d(np.polyfit(eq_x, eq_y, 12))
f_inv = inversefunc(f)
```

```
# McCabe-Thiele diagram
fig = plt.figure(figsize=[6, 6])
ax = fig.add_subplot()
plt.plot(x_values, x_values, label="Operating line")
plt.scatter(eq_x, eq_y, marker="x", c="grey", label="VLE-data")
plt.vlines(x_B, 0, f(x_B), linestyles="--", colors="grey")
plt.vlines(x_D, 0, f(x_D), linestyles="--", colors="grey")
plt.plot(x_values, f(x_values), label="Equilibrium line")
number_of_stages = draw_stairs_from_top(x_D, x_B, f_inv, op_line)
plt.xlim(0, 1)
plt.ylim(0, 1)
fig.subplots_adjust(top=0.85)
ax.text(0.3, 0.2, f"Number of stages={number_of_stages:.2f}", fontsize=12)
ax.text((x_B + 0.01), 0.01, r'$x_B$', fontsize=9, c="grey")
ax.text((x_D + 0.01), 0.01, r'$x_D$', fontsize=9, c="grey")
plt.xlabel(r'Liquid molar fraction, $x_{EtOH}$')
plt.ylabel(r'Vapour molar fraction, $y_{EtOH}$')
plt.savefig('McCabe-Thiele_diagram.png')
plt.legend()
plt.show()
print(f"The number of stages needed are: {number_of_stages:.2f}")
```