Separation by Distillation Columns
TKP4105

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1 Introduction

In this experiment, which was part of the course TKP4105 *Separasjonsteknikk* at NTNU, a mixture of water and 11 mol% ethanol was distilled using Oldershaw perforated plate distillation. The time it took for the separation column to reach steady state was determined, as well as the efficiency of the column as a function of the vapor velocity. The purpose of this experiment was to further look into the principles of distillation, the parameters affecting the operation of distillation columns and how to achieve optimal operating conditions.

2 Theory

2.1 Distillation

Distillation is the process of physically separating two components in a mixture. By taking advantage of differences in volatility, the components will distribute differently in the liquid and vapor phases. The Oldershaw distillation method uses a column that consists of multiple stages with perforated trays, thus the mixture will establish several vapor liquid equilibria.

2.2 Reflux

The portion of the vapor that is condensed at the top of the column and returned to the distillation column is called the reflux. When working with total reflux, all of the vapor at the top of the column is condensed and returned.

2.3 Column Efficiency

The overall column efficiency of a distillation column is defined as the ratio of ideal equilibrium stages to actual trays in the column. A distillation stage is considered ideal when the outgoing liquid and vapor phases establish an equilibrium. Thorough contact between liquid and gas is an indication of high column efficiency. The column efficiency of a tray column can be described mathematically by

$$\text{Column efficiency} = \frac{N_t - 1}{N_a} \cdot 100\%. \tag{2.3.1}$$

N_t depicts the number of ideal equilibrium stages, which is determined from a McCabe-Thiele diagram, while N_a depicts the number of actual trays in the column. The reboiler counts as one stage, which is why one stage is deducted from the numerator.

2.4 McCabe-Thiele Method

The McCabe-Thiele method is a graphical approach for determining the number of theoretical trays necessary for the distillation of a binary mixture. The method is based on the assumption of constant molar overflow, meaning that the molar flow of both the vapor and liquid phases are constant through all stages in a section of the column. Therefore, the operating line can be considered as a straight line for each given section of the distillation column.

2.5 Gas Chromatography

Gas chromatography is a method for separating and analyzing different chemical components in a sample. The components are dissolved in a solvent, vaporized and distributed between a stationary and a mobile phase. This distribution is caused by differences in volatility. Components with higher volatility will generally have a lower distribution in the stationary phase, and thus reach the detector faster. The detector generates a chromatogram, displaying the detector signal intensity as a function of time. The area under each peak in the chromatogram correlates to the amount of each component. The concentration of a compound can be determined by comparing the peak area with that of a compound of known concentration.

3 Experimental

3.1 Column Startup

After making sure that the top and bottom distillate tap lines were closed, the column was filled with a water-ethanol-mixture (5800 mL), such that $X_{\mathrm{EtOH}} = 0.11$ (1723.4 mL ethanol and 4075.7 mL water). The temperature was set to 105 °C and the boiler's power duty was set to 50 %. When the vapor stream started to condense, a timer was started.

3.2 Time Required to Reach Steady State

After the vapor stream had started condensing and a timer was started, samples were collected from the top distillate tap line every 5 minutes until 12 samples were collected. In addition, one sample was taken from the bottom distillate tap line after the 12 initial samples were collected. The pump flow rate and the temperature at the top of the distillation column was registered. The 13 samples were analyzed using gas chromatography to determine their composition, and thereby determine the time required to reach steady state.

3.3 Efficiency vs. Vapor Velocity

The reboiler's power duty was set to 40 %, and 20 mL samples were taken from the top and bottom distillate tap lines after the column reached steady state. This was repeated for reboiler power duties of 60 % and 70 %. The 6 samples were analyzed using gas chromatography to determine their composition, and thereby to determine vapor velocity and column efficiency.

4 Results

4.1 Exercise 1: Time Required to Reach Steady State Condition

The data collected from the first exercise is presented in table 4.1.1. The composition of the samples was found using gas chromatography. The mole fraction of ethanol in the samples was calculated as shown in appendix A.2.

Table 4.1.1: Volumetric and mole fraction of ethanol in the samples taken from the top of the distillation column at different times.

Time [min]	Composition [vol%]	Mole fraction
5	0.8432	0.6246
10	0.8680	0.6705
15	0.8753	0.6848
20	0.7888	0.5361
25	0.8632	0.6613
30	0.8867	0.7078
35	0.9402	0.8295
40	0.9279	0.7993
45	0.9046	0.7458
50	0.8958	0.7268
55	0.8859	0.7061
60	0.8773	0.6887

Figure 4.1.1 shows the molar fraction of ethanol in the distillate samples plotted against sample time. The fourth sample, i.e. the sample taken after 20 minutes, was disregarded because it deviated too much from an acceptable value.

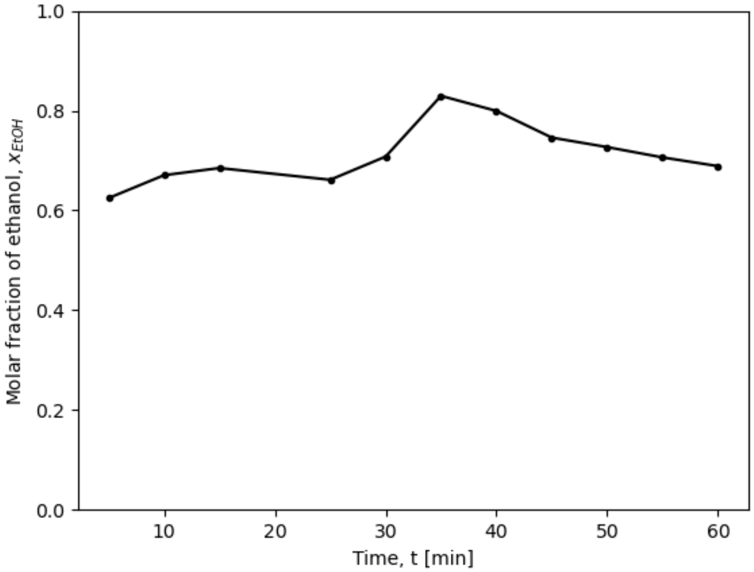


Figure 4.1.1: The molar fraction of ethanol in the distillate top samples plotted against sample time.

4.2 Exercise 2: Efficiency vs. Vapor Velocity

The calculated ethanol mole fractions for top and bottom compositions with different power settings are presented in table 4.2.1. For 60 % power duty, values from group B27 were used.

Table 4.2.1: Ethanol mole fractions for top and bottom compositions for different power duties.

Power duty [%]	x_{top}	x_{bottom}
40	0.6917	0.0779
50	0.6887	0.0895
60	0.7730	0.0521
70	0.7322	0.0794

4.2.1 McCabe-Thiele Diagrams

Figures 4.2.1.1, 4.2.1.2, 4.2.1.3 and 4.2.1.4 show the McCabe-Thiele diagrams that were made using vapor-liquid equilibrium data[1] along with the mole fractions in 4.2.1.

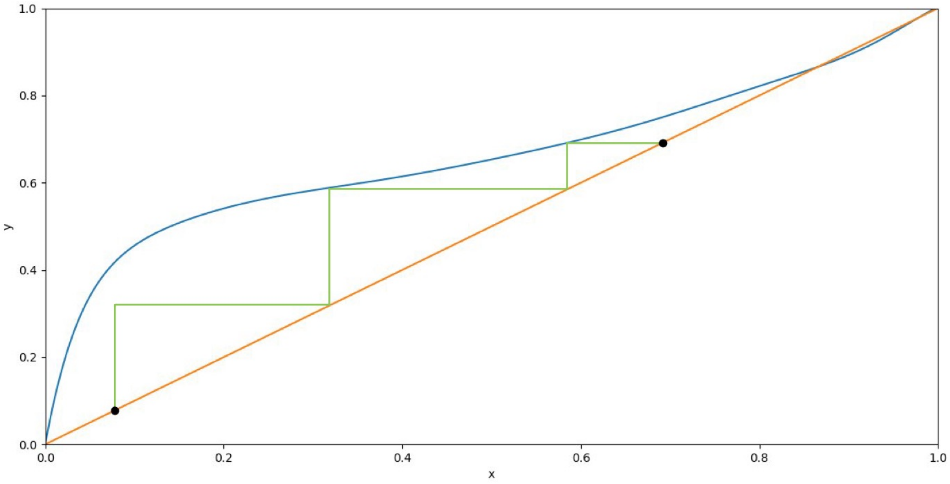


Figure 4.2.1.1: McCabe-Thiele diagram for steady state measurement at 40% power duty, with ethanol mole fractions $x_{top} = 0.6917$ and $x_{bottom} = 0.0779$. The blue line is the equilibrium line, and the orange line is the operating line y=x. The green lines show the theoretical stages.

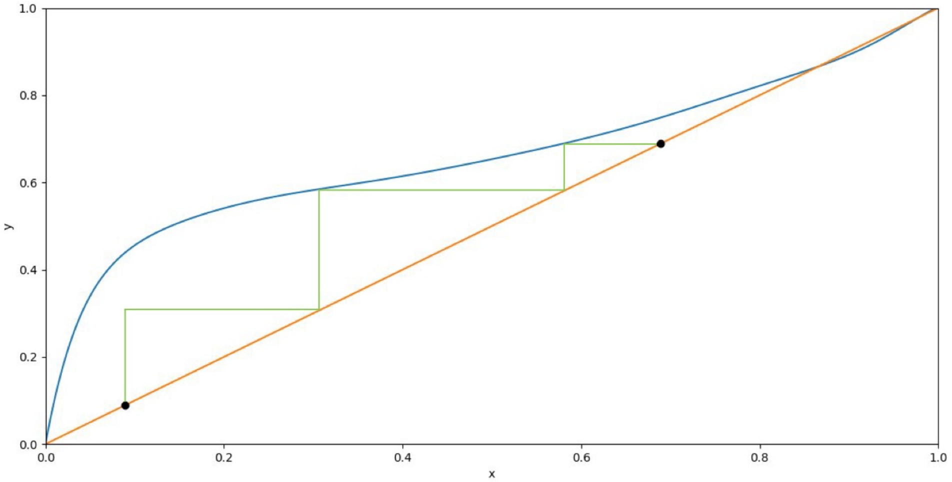


Figure 4.2.1.2: McCabe-Thiele diagram for steady state measurement at 50% power duty, with ethanol mole fractions $x_{top} = 0.6887$ and $x_{bottom} = 0.0895$. The blue line is the equilibrium line, and the orange line is the operating line y=x. The green lines show the theoretical stages.

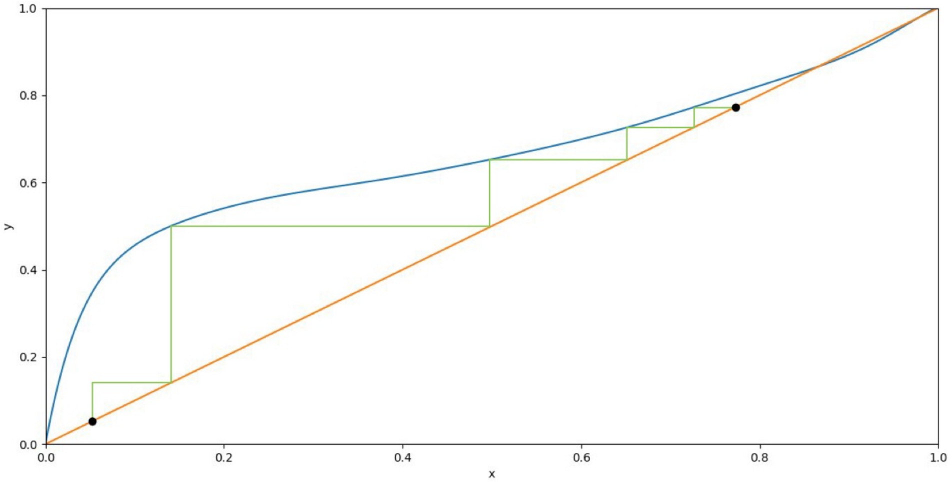


Figure 4.2.1.3: McCabe-Thiele diagram for steady state measurement at 60% power duty, with ethanol mole fractions $x_{top} = 0.7730$ and $x_{bottom} = 0.0521$. The blue line is the equilibrium line, and the orange line is the operating line y=x. The green lines show the theoretical stages.

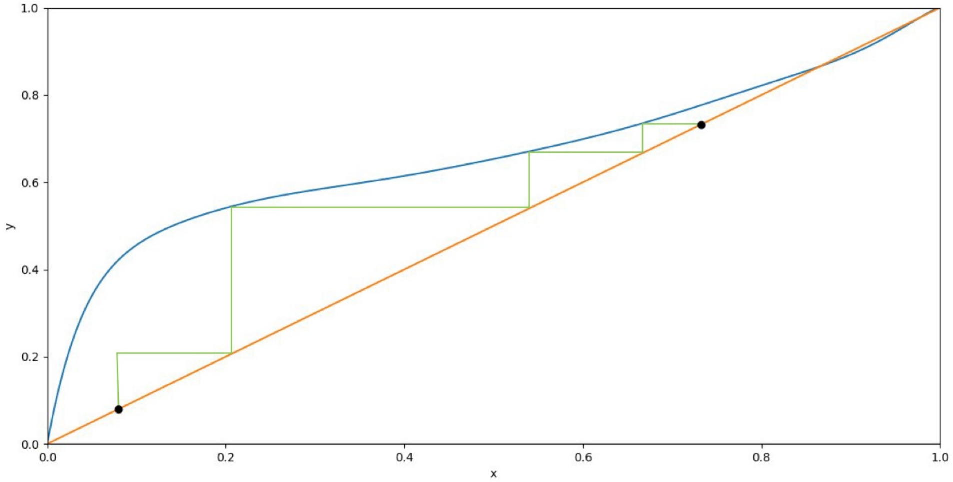


Figure 4.2.1.4: McCabe-Thiele diagram for steady state measurement at 70% power duty, with ethanol mole fractions $x_{top} = 0.7322$ and $x_{bottom} = 0.0794$. The blue line is the equilibrium line, and the orange line is the operating line y=x. The green lines show the theoretical stages.

4.2.2 Theoretical stages and column efficiency

The theoretical stages from McCabe-Thiele for the different power settings are presented in table 4.2.2.1, along with their respecitve column efficiencies calculated from equation (2.3.1).

Table 4.2.2.1: The theoretical number of stages from McCabe-Thiele diagrams and total column efficiency for different power duties.

Power duty [%]	Theoretical stages	Column efficiency [%]
40	2.85	12.33
50	2.79	11.93
60	4.68	24.53
70	3.71	18.07

A plot of total column efficiency as a function of vapor velocity is shown in figure 4.2.2.1.

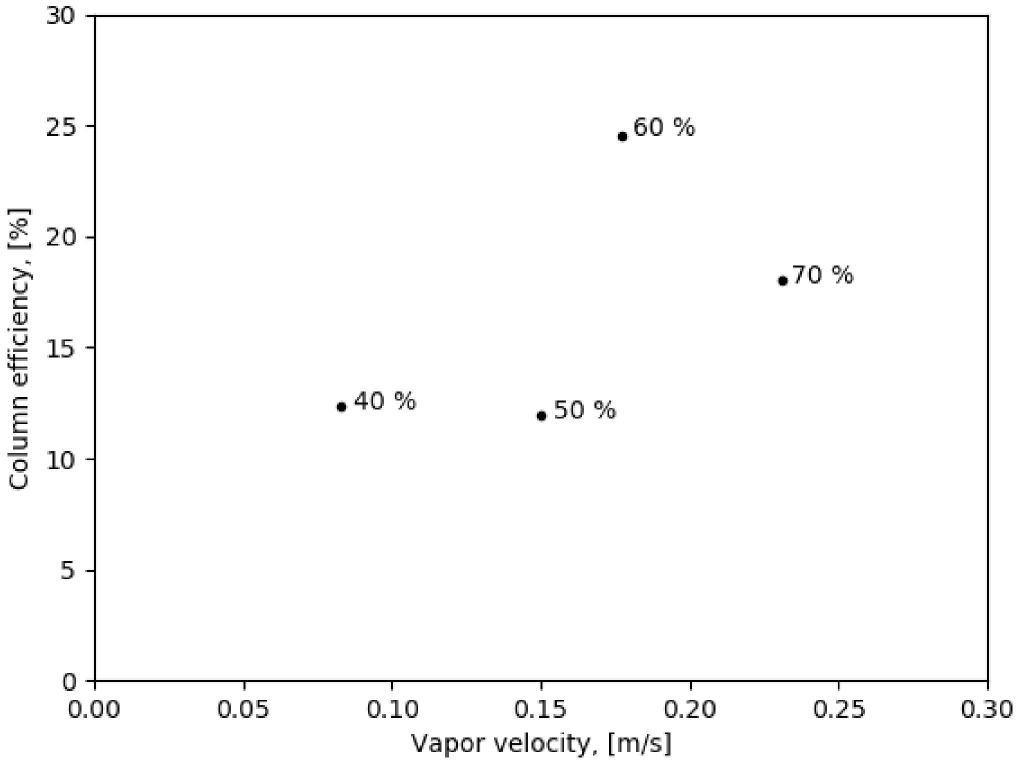


Figure 4.2.2.1: Total column efficiency as a function of vapor velocity.

5 Discussion

5.1 Exercise 1: Time Required to Reach Steady State Condition

Figure 4.1.1 shows a gradually increasing mole fraction of ethanol for the first three samples. The fourth sample, taken after 20 minutes, was disregarded because the data deviated too much from an acceptable value. The mole fraction continues to increase until it peaks at the seventh sample, i.e. after 35 minutes. After this, the mole fraction gradually decreases with every sample. These sample mole fractions are, however, the most consistent. There is no obvious point at which the system reaches steady state, but the sample mole fractions are most consistent after 45 minutes. These results deviate somewhat from what is expected. The mole fraction of ethanol should rise quickly in the beginning, before stabilizing after a while when the column reaches steady state. There are a couple of likely sources of error associated with this experiment. When preparing the samples for GC-analysis, even very small variations in measuring and mixing can cause significant fluctuations in the results. In addition, the samples were left uncovered while waiting for the GC-analysis, which may have caused some ethanol to evaporate.

5.2 Exercise 2: Efficiency vs. Vapor Velocity

In theory, a higher power duty yields a higher reflux rate, which again gives a cleaner distillation product. This means that the required number of trays decreases for higher power duties, which is why the total column efficiency should go down when the power duty is increased. However, as seen from the values in table 4.2.2.1, there is no clear trend for the column efficiency in this experiment. The column efficiency decreases from 40 % to 50 % power duty, as well as from 60 % to 70 %, but makes a big positive jump from 50 % to 60 %. One source of error here could be that the sample that was borrowed from group B27 (60 % power duty) was taken after 45 minutes, when the GC analysis showed that the system did not reach steady state until 55 or 60 minutes. This was done because the sample for 60 % in this experiment gave an ethanol mole fraction equal to 1.31, which is impossible and therefore an invalid result.

In figure 4.2.2.1, the vapor velocity is seen to rise steadily when increasing the power duty. This fits well with the theory; more power in the reboiler leads to a higher volume flow, and a higher volume flow leads to a higher vapor velocity, as seen in equation A.2.4. When calculating the vapor velocities, ideal gas and column pressure equal to 1 bar were assumed. Since the vapor condensates continuously during steady state, the gas will not accumulate and increase the pressure significantly.

References

[1] J. Gmehling and U. Onken. *Vapor-liquid Equilibrium Data Collection: Aqueous-organic systems.* Dechema, 1th edition, 1977.

[2] G. Aylward and T. Findlay. *SI Chemical Data.* John Wiley & Sons Australia, Ltd, 7th edition, 2014.

A Calculations

A.1 Calculating the Volumetric Composition of the Water-Ethanol-Mixture

The physical properties used when calculating the volumetric composition of the water-ethanol-mixture are presented in table 4.

Table 4: Physical data used for calculations [2].

Compound	M [g mol^{-1}]	ρ [g cm^{-3}]	x
EtOH	46.070	0.789	0.11
H_2O	18.016	0.997	-

From a solution of 96 vol.% ethanol, a solution of 11 mol% ethanol was to be made.
The mole fraction of ethanol in the water-ethanol-mixture is given by

$$x_{\mathrm{EtOH}} = \frac{n_{\mathrm{EtOH}}}{n_{\mathrm{EtOH}} + n_{\mathrm{H_2O}}}. \tag{A.1.1}$$

The number of moles of ethanol is given by

$$n_{\mathrm{EtOH}} = \frac{V_{\mathrm{EtOH}} \cdot \rho_{\mathrm{EtOH}}}{M_{\mathrm{EtOH}}}, \tag{A.1.2}$$

and similarly the number of moles of water is given by

$$n_{\mathrm{H_2O}} = \frac{V_{\mathrm{H_2O}} \cdot \rho_{\mathrm{H_2O}}}{M_{\mathrm{H_2O}}}. \tag{A.1.3}$$

Substitution of equation (A.1.2) and (A.1.3) into equation (A.2.1), gives

$$x_{\mathrm{EtOH}} = \frac{\frac{V_{\mathrm{EtOH}} \cdot \rho_{\mathrm{EtOH}}}{M_{\mathrm{EtOH}}}}{\frac{V_{\mathrm{EtOH}} \cdot \rho_{\mathrm{EtOH}}}{M_{\mathrm{EtOH}}} + \frac{V_{\mathrm{H_2O}} \cdot \rho_{\mathrm{H_2O}}}{M_{\mathrm{H_2O}}}}. \tag{A.1.4}$$

The volume of water is given by $V_{\mathrm{H_2O}} = V_{TOT} - V_{\mathrm{EtOH}}$, and substitution of this into equation (A.1.4) gives

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

Inserting the physical data from table 4 into equation (A.1.5), the volume of 100 vol.% ethanol was found to be

$$V_{\mathrm{EtOH,100\%}} = 1655.3\mathrm{mL}.$$

Converting the volume of 100 vol.% ethanol into 96 vol.% ethanol gave

$$V_{\mathrm{EtOH,96\%}} = \frac{V_{\mathrm{EtOH,100\%}}}{0.96} = \underline{1724.3\mathrm{mL}}.$$

Finally, the volume of water was calculated by

$$V_{\mathrm{H_2O}} = V_{TOT} - V_{\mathrm{EtOH,96\%}} = 5800\mathrm{mL} - 1724.3\mathrm{mL} = \underline{4075.7\mathrm{mL}}.$$

A.2 Calculating the Mole Fraction of Ethanol

The mole fraction of ethanol in the distillate is given by

$$x_{\mathrm{EtOH}} = \frac{n_{\mathrm{EtOH}}}{n_{\mathrm{EtOH}} + n_{\mathrm{H_2O}}}. \tag{A.2.1}$$

The number of moles of ethanol and water is given by

$$\begin{aligned} n_{\mathrm{EtOH}} &= \frac{V_{\mathrm{EtOH}} \cdot \rho_{\mathrm{EtOH}}}{M_{\mathrm{EtOH}}} \\ n_{\mathrm{H_2O}} &= \frac{V_{\mathrm{H_2O}} \cdot \rho_{\mathrm{H_2O}}}{M_{\mathrm{H_2O}}}. \end{aligned} \tag{A.2.2}$$

Using the sample compositions given in vol% of ethanol by the gas chromatograph, the volume of pure ethanol and pure water in the sample was calculated by

$$\begin{aligned} V_{\mathrm{EtOH}} &= vol\,\%_{\mathrm{EtOH}} \cdot V_{sample} \\ V_{\mathrm{H_2O}} &= (1 - vol\,\%_{\mathrm{EtOH}}) \cdot V_{sample}, \end{aligned} \tag{A.2.3}$$

where V_{sample} is the measured volume of the sample that was analyzed.

Finally, the number of moles of ethanol and water was calculated from equation (A.2.2), and the values put into equation (A.2.1) to find the mole fractions of ethanol.

A.2.1 Example Calculation

The volume of distillate analyzed by the gas chromatograph was measured out to be 500 µL, which equals $500 \cdot 10^{-6}$ L. For sample 1, i.e. the sample taken after 5 minutes, the volume fraction of ethanol was found by the gas chromatograph to be 0.8432. This yields the following volumes of pure components

$$\begin{aligned} V_{\mathrm{EtOH}} &= 500 \cdot 10^{-6}\,\mathrm{L} \cdot 0.8432 = 4.216 \cdot 10^{-4}\,\mathrm{L} = \underline{0.4216\,\mathrm{mL}} \\ V_{\mathrm{H_2O}} &= 500 \cdot 10^{-6}\,\mathrm{L} \cdot (1 - 0.8432) = \underline{0.0784\mathrm{mL}}. \end{aligned}$$

Using $\rho_{\mathrm{EtOH}} = 0.789$ g/mL and $\rho_{\mathrm{H_2O}} = 0.997$ g/mL, the weight of the pure components is calculated to be

$$\begin{aligned} m_{\mathrm{EtOH}} &= 0.789\,\mathrm{g/mL} \cdot 0.4216\mathrm{mL} = 0.3326\mathrm{g} \\ m_{\mathrm{H_2O}} &= 0.997\,\mathrm{g/mL} \cdot 0.0784\mathrm{mL} = 0.07816\mathrm{g}. \end{aligned}$$

From this, the moles of ethanol and water respecitvely is calculated to be

$$\begin{aligned} n_{\mathrm{EtOH}} &= \frac{0.3326\,\mathrm{g}}{46.07\,\mathrm{g/mol}} = 7.2194 \cdot 10^{-3}\,\mathrm{mol} \\ n_{\mathrm{H_2O}} &= \frac{0.07816\,\mathrm{g}}{18.016\,\mathrm{g/mol}} = 4.3384 \cdot 10^{-3}\,\mathrm{mol}. \end{aligned}$$

Finally, the mole fraction of ethanol is found to be

$$x_{\text{EtOH}} = \frac{7.2194 \cdot 10^{-3}\,\text{mol}}{7.2194 \cdot 10^{-3}\,\text{mol} + 4.3384 \cdot 10^{-3}\,\text{mol}} = \underline{0.6246}.$$

A.2.2 Vapor Velocity

The vapor velocity is calculated by

$$v = \frac{\dot{V}_{gas}}{A}, \tag{A.2.4}$$

where $\dot{V}_{gas}$ is the volume rate of the gas and A is the cross section area of the column. Considering the equation of state for an ideal gas,

$$pV = nRT, \tag{A.2.5}$$

where p is pressure, V is volume, n is the number of moles, R is the universal gas constant and T is the temperature, an equation for $\dot{V}_{gas}$ is derived by substituting n with the molar flow rate, $\dot{n}$:

$$\dot{V}_{gas} = \frac{\dot{n}RT}{P}. \tag{A.2.6}$$

Inserting equation (A.2.6) into equation (A.2.4), the vapor velocity can be calculated from

$$v = \frac{\dot{n}RT}{PA}. \tag{A.2.7}$$

The molar flow rate, $\dot{n}$, can be calculated from

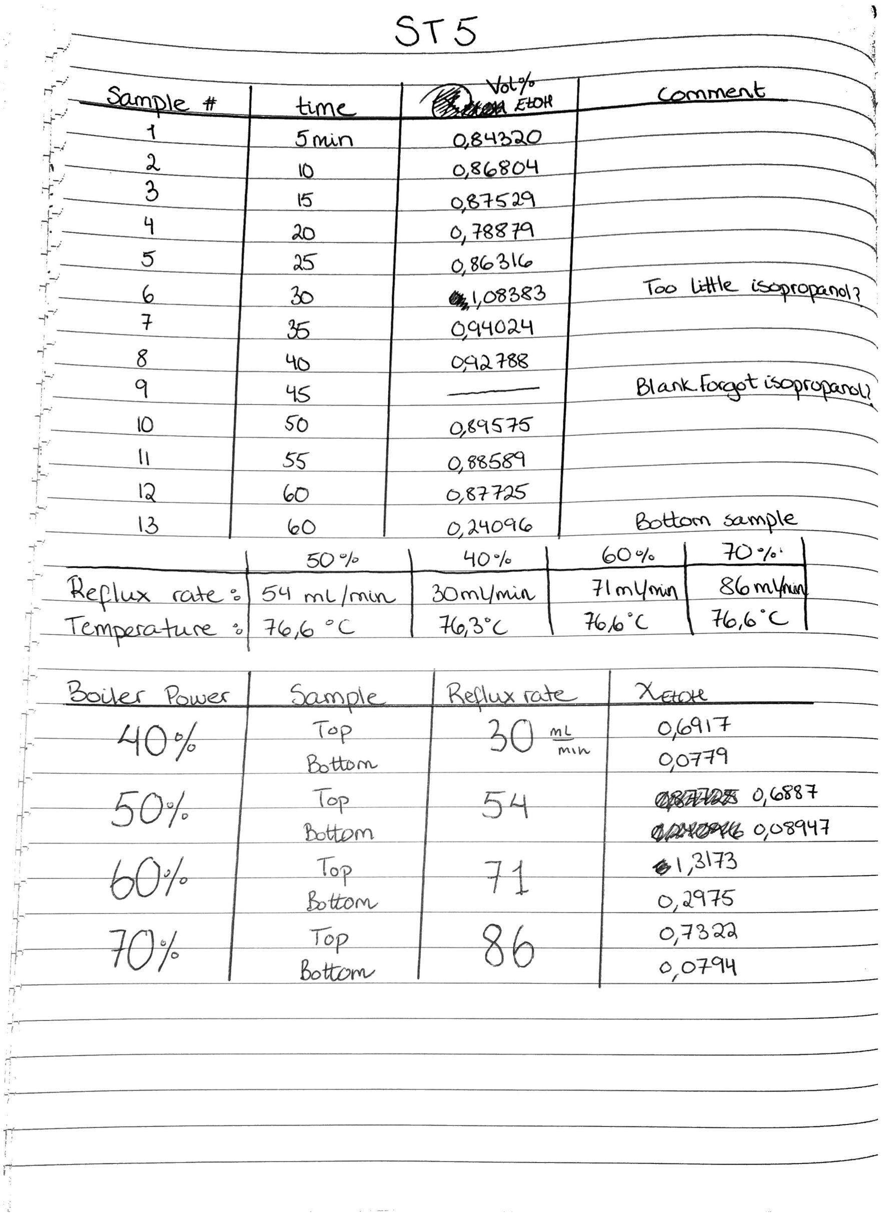
$$\dot{n}_{tot} = \frac{\dot{m}_{tot}}{x_{\text{EtOH}} \cdot M_{\text{EtOH}} + (1 - x_{\text{EtOH}}) \cdot M_{\text{H}_2\text{O}}}. \tag{A.2.8}$$

Due to total reflux, $\dot{m} = \rho \cdot \dot{V}_{tot}$, so this gives

$$\dot{n}_{tot} = \frac{\rho_{distillate} \cdot \dot{V}_{tot}}{x_{\text{EtOH}} \cdot M_{\text{EtOH}} + (1 - x_{\text{EtOH}}) \cdot M_{\text{H}_2\text{O}}}. \tag{A.2.9}$$

B Lab Journal

A photocopy of the lab journal is shown in figure B.1.



ST5

Sample #	time	Vol% EtOH	Comment
1	5min	0,84320	
2	10	0,86804	
3	15	0,87529	
4	20	0,78879	
5	25	0,86316	
6	30	1,08383	Too little isopropanol?
7	35	0,94024	
8	40	0,92788	
9	45	———	Blank. Forgot isopropanol?
10	50	0,89575	
11	55	0,88589	
12	60	0,87725	
13	60	0,24096	Bottom sample

	50%	40%	60%	70%
Reflux rate :	54 mL/min	30mL/min	71mL/min	86mL/min
Temperature :	76,6 °C	76,3°C	76,6°C	76,6°C

Boiler Power	Sample	Reflux rate	x_{EtOH}
40%	Top	30 mL/min	0,6917
	Bottom		0,0779
50%	Top	54	0,6887
	Bottom		0,08947
60%	Top	71	1,3173
	Bottom		0,2975
70%	Top	86	0,7322
	Bottom		0,0794

Figure B.1: Photocopy of the lab journal used during the experiment.

C Python Code

```
"""
Created on Fri 24.09.2021 12:54:10

@authors: Eva Aunet & Anine Bodsberg

"""

import numpy as np
import matplotlib.pyplot as plt

# Plot molar fraction of distillate vs time
time = [5, 10, 15, 25, 30, 35, 40, 45, 50, 55, 60]
molar_frac = [0.6246, 0.6705, 0.6848, 0.6613, 0.7078, 0.8295, 0.7993, 0.7458, 0.7268, 0.7061, 0.6887]

plt.plot(time, molar_frac, linestyle='-', marker='.', color='black')
plt.xlabel('Time, t [min]')
plt.ylabel('Molar fraction of ethanol, $x_{EtOH}$')
plt.ylim([0, 1])
plt.show()

# Constants needed in calculations

R = 8.314  # J/Kmol
P = 1 * 10 ** 5  # Pa
A = 3.8485 * 10 ** (-3)  # m^2
rho_d = 0.8229  # g/cm^3, density of distillate
M_E = 46.07  # g/mol
M_W = 18.016  # g/mol

# Temperature at the top of the column at different power settings
T = np.array([76.3, 76.6, 76.6, 76.6]) + 273.15  # Kelvin

# Total volume flow at different power settings
V_tot = np.array([30, 54, 68, 86])  # mL/min

# Mole fractions of ethanol in top sample for different power settings
X_E = np.array([0.69174, 0.68865, 0.7730, 0.73221])


# Calculating the molar flows for different power settings
def molar_flow(rho, V, X, M_ethanol, M_water):
    n_flow = (rho * V) / ((X * M_ethanol) + ((1 - X) * M_water))
    return n_flow


n = molar_flow(rho_d, V_tot, X_E, M_E, M_W)  # mol/min


# Calculating the vapor velocity
def vapor_velocity(n_flow, R, T, P, A):
    v_v = (n_flow * R * T) / (P * A * 60)
    return v_v
```

```
v = vapor_velocity(n, R, T, P, A)  # m/s
print('The molar flows are:', n)
print('The vapor velocities are:', v)

column_efficiency = np.array([12.33, 11.93, 24.53, 18.07])

plt.plot(v, column_efficiency, '.', color='black')
plt.text(0.087, 12.20, '40 %')
plt.text(0.154, 11.80, '50 %')
plt.text(0.181, 24.50, '60 %')
plt.text(0.234, 17.90, '70 %')
plt.xlim(0, 0.30)
plt.ylim(0, 30)
plt.xlabel('Vapor velocity, [m/s]')
plt.ylabel('Column efficiency, [%]')
plt.show()
"""
25.09.2021
TKP4105 ST5
Eva Aunet & Anine Bodsberg
"""

import numpy as np
import matplotlib.pyplot as plt

# Vapor-liquid equilibrium data
x_VLE = [0, 0.0160, 0.0315, 0.0600, 0.0855, 0.1465, 0.2060, 0.2360, 0.3495,
         0.4675, 0.4875, 0.5800, 0.6525, 0.7000, 0.7175, 0.7890, 0.8420, 0.8749,
         0.8967, 0.9485, 0.9727, 1.0000]
y_VLE = [0, 0.1470, 0.2505, 0.3765, 0.4300, 0.5005, 0.5415, 0.5600, 0.5945,
         0.6410, 0.6425, 0.6890, 0.7250, 0.7495, 0.7680, 0.8111, 0.8488, 0.8768,
         0.8793, 0.9440, 0.9692, 1.0000]


# Molar fractions for top and bottom compositions, [40%, 50%, 60%, 70%]
x_top = [0.6917, 0.6887, 1.3173, 0.7322]
x_btm = [0.0779, 0.0895, 0.2975, 0.0794]


# Equilibrium line
def eq_line(x):
    a = 10
    eq_line = 0
    coeff = np.polyfit(x_VLE, y_VLE, a)
    for i in range(len(coeff) - 1):
        eq_line += coeff[i] * x ** (a - i)
    return eq_line


# Diagonal xy_line
def xy_line(x):
    y = x
    return y
```

```
# Plotting the graphs
for i in range(0, len(x_top)):
    x = np.linspace(0, 1, 1000)
    plt.plot(x, eq_line(x))
    plt.plot(x, xy_line(x))
    plt.xlim(0, 1)
    plt.ylim(0, 1)
    plt.xlabel('x')
    plt.ylabel('y')
    plt.plot(x_top[i], xy_line(x_top[i]), 'o', color='black')
    plt.plot(x_btm[i], xy_line(x_btm[i]), 'o', color='black')
    plt.show()
```

D McCabe-Thiele Diagram

The McCabe-Thiele diagram for the 40 % power duty was drawn by hand on a mm-scale paper in addition to the plot shown in figure 4.2.1.1. The drawing is shown in figure D.1. The data used to plot the equlibrium line is taken from *Vapor-liquid Equilibrium Data Collection*[1]. Since total reflux is assumed, the upper and lower operating line are both equal to $y = x$. The number of theoretical stages for the 40 % power duty was found to be 2.97.

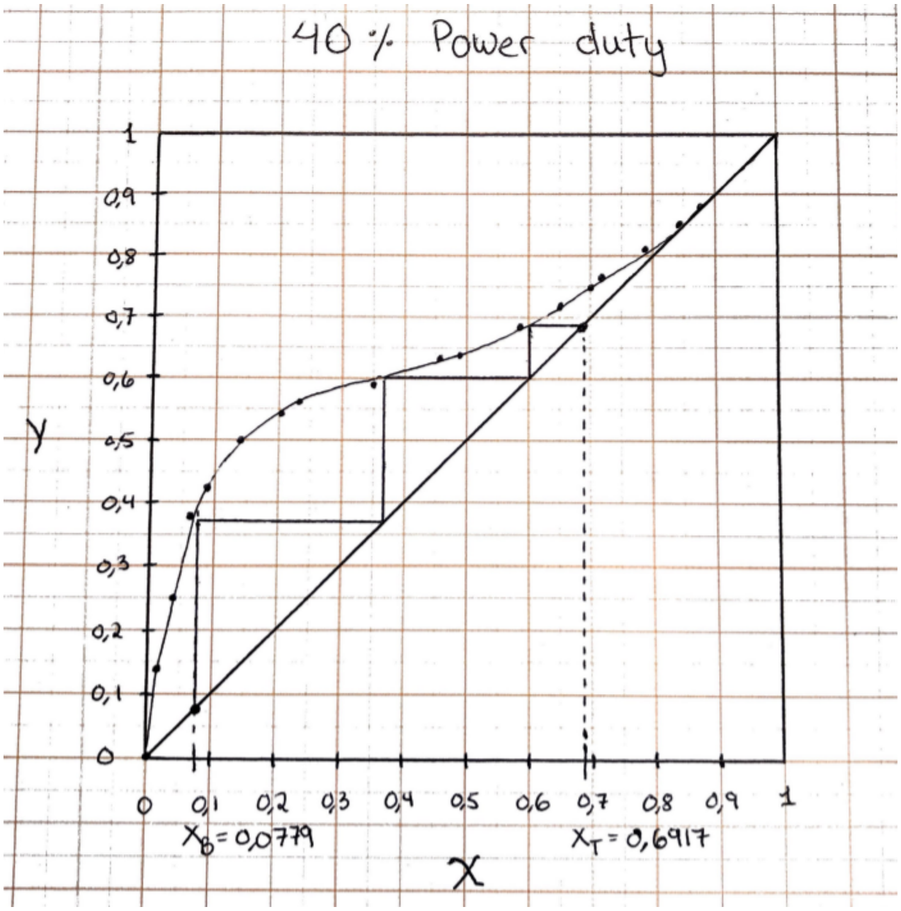


Figure D.1: McCabe-Thiele diagram for 40 % power duty, drawn by hand on mm-scale paper.