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FELLESLAB

ST4 - Separation by Distillation Columns

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October, 2021

1 Introduction

In this experiments, a raschig-ring distillation is going to be performed on a a mixture of 10 mol% ethanol and water. The goal of the experiment is to determine the time it takes the column to reach steady state conditions, as well as determining the efficiency of the column as a function of the vapour velocity. The purpose of this is to obtain an understanding of the principles of distillation, of how to achieve optimal operating conditions, and of the parameters affecting the operation of a distillation column.

2 Theory

2.1 Distillation

The process of distillation involve separating two or more products from a mixture, on the basis of the products having different boiling points. A mixture of components, either in gas or liquid phase is fed into distillation column, and when heated up the components will distribute differently in the liquid and vapour phase.

In a packed distillation column the gas-liquid contact is continuous, not divided into stages.[1] Instead of stages the column is filled with packing, which gives the vapour and gas a high surface area to react, and increases the distillation efficiency.

2.2 Reflux

Vapour at the top of the column is reverted to the distillation column, and this product is called reflux. The amount of condensed liquid returned to the column is usually calculated as the reflux ratio. In this experiment, total reflux is used, meaning that all the vapour is returned to the column.

2.3 Column Efficiency

The overall column efficiency of a distillation column is defined as the ratio of ideal equilibrium stages to the actual number of trays present in the column. If an equilibrium is established between the outgoing vapour and liquid phase, the distillation can be considered ideal. Thorough contact between the vapour and liquid phase indicates high column efficiency.

For packed column the number of trays are assumed equivalent to the height of a theoretical plate (HETP), where HETP is the height of packing corresponding to separation by theoretical plates. For packed column, the height of a theoretical plate (HETP) is used to estimate the number of trays, which is related to efficiency. HETP is the height of packing necessary to do the same separation as a theoretical plate.

2.4 McCabe-Thiele Method

The McGabe-Thiele method is a method used to graphically determine the number of theoretical trays needed for distillation of a binary mixture. To use this method, it must be assumed constant molar overflow, which means that the molar flow of both the vapour and the liquid phase are constant through all stages in a section of the column. Thus, the operating line can be considered linear, for each given section of the distillation column.

2.5 Gas Chromatography

Gas chromatography is a method used for separating and analysing different chemical components in a sample. The components are dissolved in a solvent and vaporised, before they can be distributed between a mobile and a stationary phase. This distribution can happen because the components have different volatilities. In general, the component with higher volatility will have a higher distribution in the mobile phase, and therefore this components will move at a faster pace. Thus the components can be separated and analysed with gas chromatography. The concentration of each component can be determined by comparing the peak area from the gas chromatography with that of a known sample of the same component.

3 Experimental Procedure[2]

3.1 Column setup

The computer was switched on, and the cooling water for the column was turned on to an appropriate amount. All taps were closed prior to filling the column with 1600 mL ethanol and 4200 deionized water, and the reflux was set to total reflux. The temperature was set to 105°C, and the boiler duty was set to 50 %. A timer was set as the first drop of condensate was observed.

3.2 Exercise 1: Time Required to Reach Steady State Condition

A sample was taken every 5 minutes, until 12 samples were taken. When sample number 12 was take, an additional sample from the bottom of the column was also taken. The temperature and pump flow rate was noted down. Then the samples were analyzed in the GC to calculate how long it took the system to reach steady state.

3.3 Exercise 2: Efficiency vs. Vapour Velocity

The boiler duty was set to 40 %, and the system was left to reach steady state, which took about 15 minutes. Two samples were then taken, one from the top and one from the bottom. Temperature and pump flow was noted down. This step was repeated for boiler duty of 35 % and 30 %. The samples were analyzed in the GC.

3.4 Column Shutdown

The heater was turned off. The content in the column was left to cool down, before it was emptied, and cooling water was turned off.

3.5 Gas Chromatography Analysis

Samples for the GC was prepared by mixing 500 µL of ethanol sample with 250 µL of isopropanol in a glass vial. The vials were sealed properly with caps. Then analyzed by using gas chromatography.

4 Results

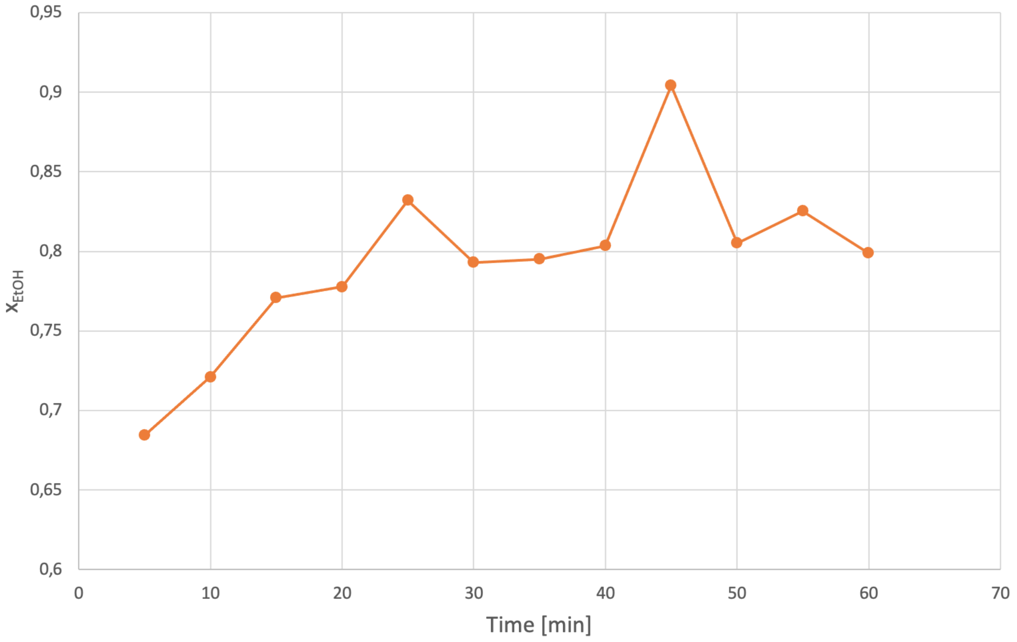
4.1 Exercise 1: Time Required for Reaching Steady State Condition

Table 4.1 shows the composition of the samples taken from the top at the given time points. The volume percentage of ethanol, vol$\%_{EtOH}$, was found from the GC analysis, and the molar fraction, x_{EtOH}, was calculated from equation B.4.

Tabell 4.1: Volumetric and molar fraction of ethanol from distillate at the given time points.

Time [min]	vol$\%_{EtOH}$	x_{EtOH}
5	0.87513	0.68443
10	0.89310	0.72110
15	0.91573	0.77080
20	0.91877	0.77780
25	0.94122	0.83209
30	0.92532	0.79315
35	0.92613	0.79508
40	0.92969	0.80362
45	0.96827	0.90425
50	0.93037	0.80526
55	0.93849	0.82523
60	0.92772	0.79888

Figure 4.1 show the molar fraction of ethanol as a function of time. The values used in the plot are given in table 4.1. The 12 samples were all taken within one hour, in order to determine when the column reached steady state. Boiler duty was set to 50%.



Figur 4.1: Molar fraction of ethanol as a function of time.

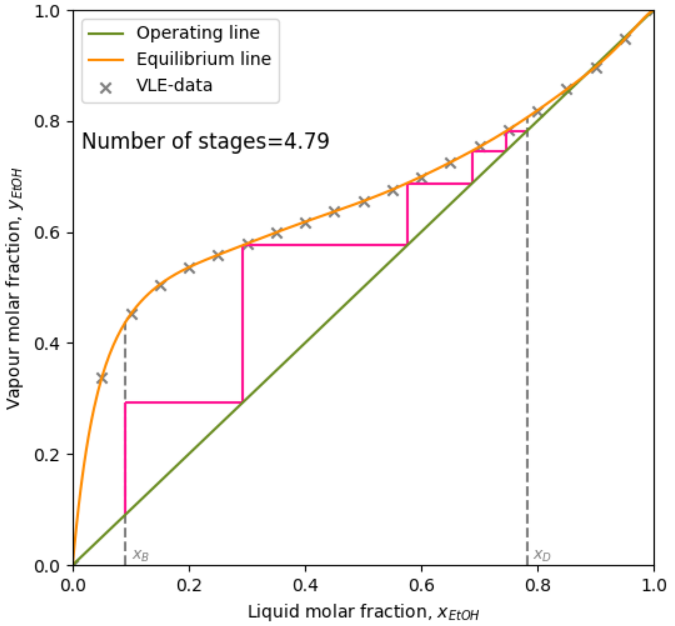
4.2 Exercise 2: Efficiency vs. Vapour Velocity

Table 4.2 shows the composition of top and bottom product at different power settings.

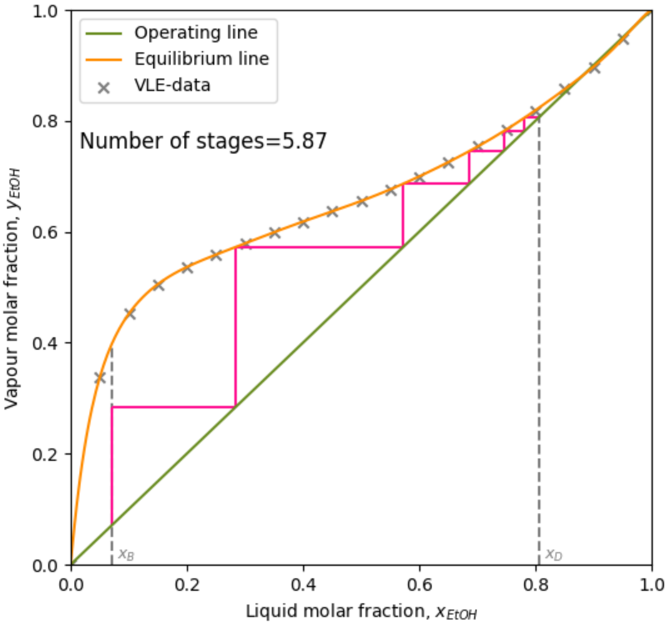
Tabell 4.2: Ethanol mole fractions for top and bottom at different power settings.

Power setting [%]	x_{top}	x_{bottom}
35	0.78184	0.09134
40	0.80543	0.06992
45	0.79289	0.07220
50	0.79888	0.07266

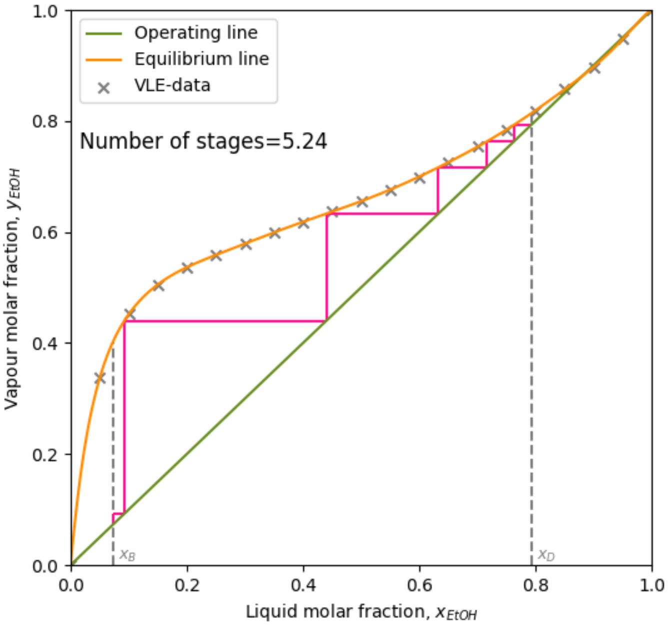
McCabe-Thiele diagrams were created for each of the four different power settings, and these are shown in figures 4.2-4.5. The diagrams are based on the top and bottom composition measured from the GC. The GC analysis gave the volumetric fractions, which were then converted to molar fractions using equation B.4. The equilibrium line was plotted using data from Vapor-Liquid Equilibrium Data Collection[3], and the operating line is y = x, because of total reflux. The ideal number of trays found using the McCabe-Thiele diagrams are shown in table 4.3.



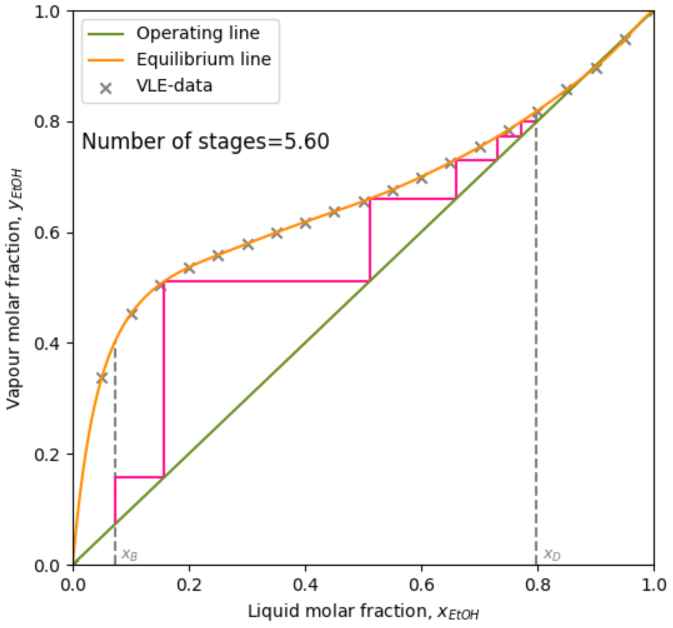
Figur 4.2: McCabe-Thiele diagram for 35% power duty. The ideal number of trays is 4.79.



Figur 4.3: McCabe-Thiele diagram for 40% power duty. The ideal number of trays is 5.87.



Figur 4.4: McCabe-Thiele diagram for 45% power duty. The ideal number of trays is 5.24.



Figur 4.5: McCabe-Thiele diagram for 50% power duty. The ideal number of trays is 5.60.

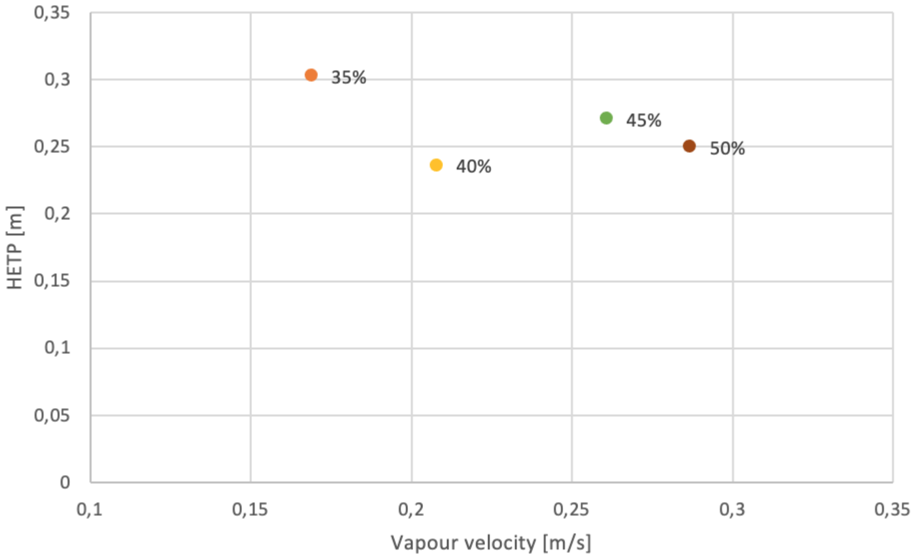
4.2.1 Efficiency and Vapour Velocity

Table 4.3 shows the calculated values for theoretical stages, HETP, and vapour velocities, for the given power duties. The HETP was calculated using B.5 and the vapour velocity was calculated using equation B.9.

Tabell 4.3: Calculated values for theoretical stages, HETP, and vapour velocities, for the given power duties.

Power duty [%]	Theoretical stages	HETP [m]	Vapour velocity [$\mathrm{m\,s^{-1}}$]
35	4.79	0.303	0.169
40	5.87	0.236	0.208
45	5.24	0.271	0.261
50	5.60	0.250	0.287

Figure 4.6 shows the vapour velocity as a function of the HETP, for each of the power duties.



Figur 4.6: Vapour velocity as a function of HETP.

5 Discussion

5.1 Exercise 1: Time Required to Reach Steady State

As shown in figure 4.1 the molar fraction of ethanol increased gradually until sample five, which was taken after 25 minutes of boiling. Thereafter, the molar fraction started to stabilize at around 80% ± 2%, except for sample number nine which deviated quite a lot from the average. Disregarding sample number nine, it is valid to assume the system reached its steady state after 30 minutes.

An explanation to why the data from sample nine deviates from the rest, may be improper GC-preparation of the sample, assuming that there is no error within the GC. Inadequate mixing of the sample, resulting in poor blend of the isopropanol and the ethanol, may have resulted in a higher yield.

5.2 Exercise 2: Efficiency vs. Vapour Velocity

In experiment 2 the vapour velocity was calculated for all of the varying power settings, and the values are shown in table 4.3. The trend shows that with increasing power duty, the vapour velocity of the gas also increased. In theory, a higher power duty would equal a higher reflux rate, which again would result in a cleaner distillate and a lower column efficiency. Even though there is no way to calculate the efficiency of a packed column, the HETP is an estimation, and the data shows a decreasing trend, and therefore agrees with the theory.

Table 4.1 shows that the sample at 40% power duty deviates, seeing that it is somewhat lower than the linear trend of power duty 35, 45 and 50%. This could come from not letting the system fully stabilize after increasing the power duty from 35 to 40%. However if this was the case, the data for 40% should have been higher, not lower. Therefore it is more likely that the deviation results from inadequate mixing of the sample at 40%. Data from the sample at 40%, shown in table 4.2, show increased values for x_{top} and decreased values for x_{bottom}, compared to the the data for samples at 35, 45, and 50%. This will have affected the McCabe-Thiele diagram for 40% power duty, as the interval ($\Delta_x = x_{top}$ - x_{bottom}) increased, which allowed a higher number of stages. An increase in number of stages has decreased the calculated HETP, which accounts for why the data point for 40% is below the linear trend in figure 4.1.

6 Conclusion

In this experiment, a raschig-ring distillation was performed, and the time required to obtain steady state was observed, as well as determining the column's efficiency based on the vapour velocity. The results show that the system reached steady state after 30 minutes, and the ethanol molar fraction stabilized at around 80%. As the theory predicted, increasing the power duty decreased the column efficiency. Deviations from this trend likely resulted from poor mixing of the sample taken at 40% power duty.

Trondheim, 29. oktober 2021

Referanser

[1] Packed distillation columns. URL `http://kkft.bme.hu/attachments/article/101/packed.pdf`.

[2] Felleslab: Distillation columns, 2011. URL `https://folk.ntnu.no/preisig/HAP_Specials/Felles_lab/Experiments/ST2-5_distillation.pdf`.

[3] J. Gmehling and U. Onken. *Vapor-Liquid Equilibrum Data Collection: Aqueous-Organic Systems*. Dechema, 1st edition, 1977.

[4] Allan G. Blackman. *Aylward and Findlay's SI chemical data*. Wiley, 7th edition, 2014.

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

A Calculations Prior to Experiment

A.1 Water and Ethanol Mixture

The physical properties used when calculating the volumetric composition of the water-ethanol-mixture are shown in table 4.1. Here Mm is the molar mass, ρ is the density, and x is the mole fraction:

Tabell A.1: Physical data for ethanol and water [4]

Component	Mm [$\mathrm{g\,mol^{-1}}$]	ρ [$\mathrm{g/cm^3}$]	x
EtOH	46.070	0.789	0.1
H_2O	18.016	0.997	-

The total volume of the mixture, V_{tot}, is 5800 mL, and can be expressed as:

$$V_{tot} = V_{\mathrm{H_2O}} + V_{EtOH}, \tag{A.1}$$

where $V_{\mathrm{H_2O}}$ and V_{EtOH} are the volumes of H_2O and ethanol respectively.

The mole fraction of ethanol in the water-ethanol-mixture is given by:

$$x_{EtOH} = \frac{n_{EtOH}}{n_{EtOH} + n_{\mathrm{H_2O}}}, \tag{A.2}$$

where n is the number of moles of the respective component.

The number of moles of ethanol and water are given by equations A.3 and A.4 respectively:

$$n_{\mathrm{H_2O}} = \frac{V_{\mathrm{H_2O}} \cdot \rho_{\mathrm{H_2O}}}{Mm_{\mathrm{H_2O}}}, \tag{A.3}$$

$$n_{EtOH} = \frac{V_{EtOH} \cdot \rho_{EtOH}}{Mm_{EtOH}}, \tag{A.4}$$

where V is the volume of the respective component.

Combining equation A.1, A.3 and A.4 gives equation A.2:

$$x_{EtOH} = \frac{\frac{V_{EtOH} \cdot \rho_{EtOH}}{Mm_{EtOH}}}{\frac{V_{EtOH} \cdot \rho_{EtOH}}{Mm_{EtOH}} + \frac{(V_{tot} - V_{EtOH}) \cdot \rho_{\mathrm{H_2O}}}{Mm_{\mathrm{H_2O}}}} \tag{A.5}$$

This equation can be solved for V_{EtOH} for 100 % etanol, by inserting the variables in 4.1. This gives:

$$V_{EtOH,100\%} = 1532.3\,\mathrm{mL}.$$

The ethanol being used in the experiment is 96%, so this has to be taken into account by dividing by 0.96. This gives a volume for 96% ethanol:

$$V_{EtOH} = 1596\,\mathrm{mL}.$$

The volume of water can then be found by equation A.1, and equals:

$$V_{\mathrm{H_2O}} = 4204\,\mathrm{mL}.$$

B Calculations for Results

B.1 Conversion of Volumetric Fraction into Molar Fraction

The molar fraction of ethanol, x_{EtOH}, can be expressed as:

$$x_{EtOH} = \frac{n_{EtOH}}{n_{tot}} = \frac{n_{EtOH}}{n_{EtOH} + n_{H_2O}}, \tag{B.1}$$

where n_{EtOH} and $n_{\mathrm{H_2O}}$ of the respective components.

To convert the volume, V_i, of a species i to number of moles, n_i, equation B.2 is used:

$$n_i = \frac{\rho_i V_i}{Mm_i} = \frac{\rho_i x_{V,i} V_{tot}}{Mm_i}. \tag{B.2}$$

Here are ρ_i, V_i and Mm_i the density, the volume and the molar mass of species i, respectively. $x_{V,i}$ is the volume fraction of i and V_{tot} is the total volume.

Inserting equation (B.2.2) into equation (B.2.1), for the species EtOH and H2O, gives the expression

The molar fraction of ethanol was calculated by inserting B.2 into B.1:

$$x_{EtOH} = \frac{\frac{\rho_{EtOH} \cdot x_{V,EtOH} \cdot V_{tot}}{Mm_{EtOH}}}{\frac{\rho_{EtOH} \cdot x_{V,EtOH} \cdot V_{tot}}{Mm_{EtOH}} + \frac{\rho_{\mathrm{H_2O}} \cdot x_{V,\mathrm{H_2O}} \cdot V_{tot}}{Mm_{\mathrm{H_2O}}}} \tag{B.3}$$

$$= \frac{x_{V,EtOH} \cdot \rho_{EtOH} \cdot Mm_{\mathrm{H_2O}}}{x_{V,EtOH}(\rho_{EtOH} \cdot Mm_{\mathrm{H_2O}} - \rho_{\mathrm{H_2O}} \cdot Mm_{EtOH}) + \rho_{\mathrm{H_2O}} + Mm_{\mathrm{H_2O}}} \tag{B.4}$$

B.2 Height Equivalent to a Theoretical Plate (HETP)

The height equivalent to a theoretical plate (HETP) is calculated by:

$$HETP = \frac{H}{N_t - 1}, \tag{B.5}$$

where H is the height of packing, which was measured to be 1.15 m, and N_t is the number of theoretical stages found from the Mccabe-Thiele diagrams. The number of theoretical stages are shown in table 4.3.

B.3 Vapour Velocity

The vapour velocity can be calculated using:

$$v = \frac{\dot{V}_{gas}}{A}, \tag{B.6}$$

where $\dot{V}_{gas}$ is the volume rate of the gas, and A is the cross-sectional area of the column.

A can be calculated by using:

$$A = \frac{\pi}{4}D^2, \tag{B.7}$$

where D is the diameter of the column, which here equals 0.05 m.

The volume rate, $\dot{V}_{gas}$, can be calculated by using the ideal gas law:

$$\dot{V}_{gas} = \frac{\dot{n}RT}{p}, \tag{B.8}$$

where $\dot{n}$ is the molar gas flow, R is the universal gas constant, T is the temperature in the reactor, and p is the pressure.

By inserting equation B.7 and B.8 into equation B.6, an expression for the vapour velocity is:

$$v = \frac{4\dot{n}RT}{\pi D^2 p}, \tag{B.9}$$

Before calculating v, the molar flow needs to be found. This is found by:

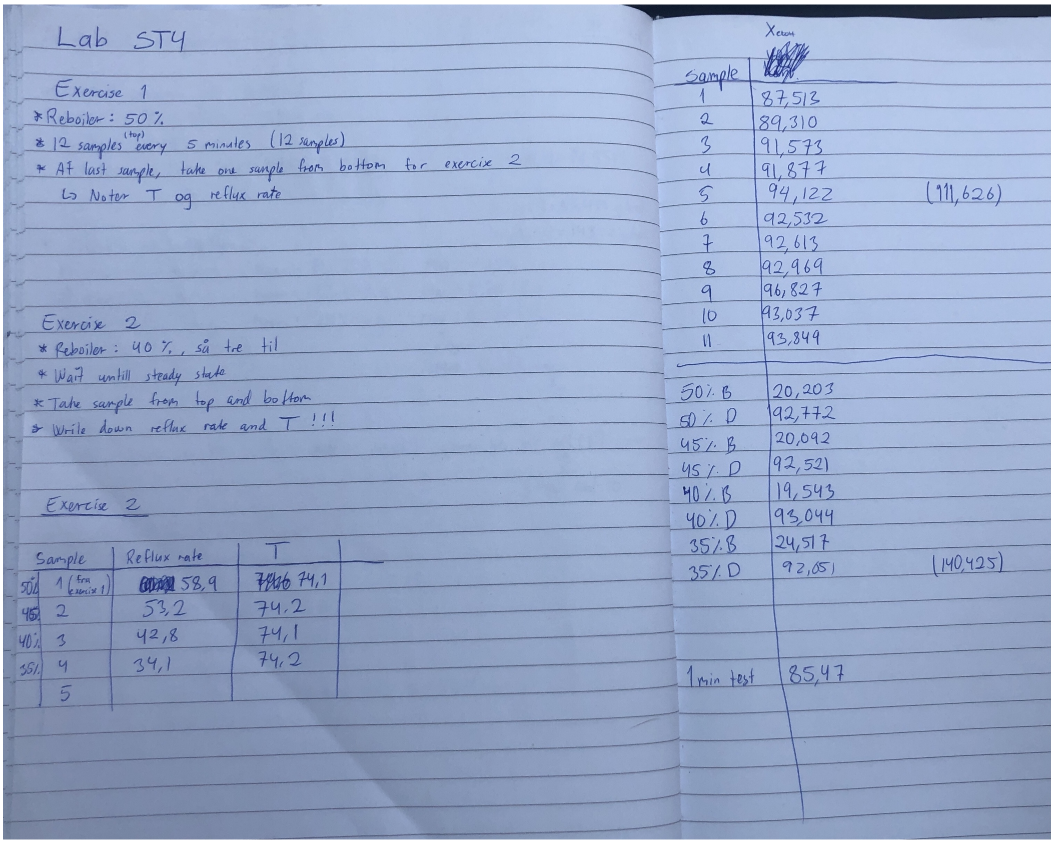
$$\dot{n} = \frac{\dot{m}}{Mm} = \frac{\dot{V} \cdot \rho_{distillate}}{x_{EtOH} \cdot Mm_{EtOH} + (1 - x_{EtOH}) \cdot Mm_{\mathrm{H_2O}}} \tag{B.10}$$

Here $\dot{V}$ is the total reflux and x_{EtOH} is the molar fraction of ethanol, and these values are shown in 4.1. $\rho_{distillate}$ is the density of the distillate, which was found using data from ethanol-water-density-composition data from Perry's handbook[5].

The vapour velocity is then calculated by putting the values into equation B.9.

C Lab Journal

Figure C.1 is a photocopy of the lab journal with notes made during the experiment.



Lab ST4

Exercise 1

* Reboiler : 50 %
* 12 samples (top) every 5 minutes (12 samples)
* At last sample, take one sample from bottom for exercise 2
↳ Noter T og reflux rate

Exercise 2

* Reboiler : 40 %, så tre til
* Wait untill steady state
* Take sample from top and bottom
* Write down reflux rate and T !!!

Exercise 2

	Sample	Reflux rate	T
50%	1 (fra exercise 1)	58,9	74,1
45%	2	53,2	74,2
40%	3	42,8	74,1
35%	4	34,1	74,2
	5		

Sample	X_{etoH}	
1	87,513	
2	89,310	
3	91,573	
4	91,877	
5	94,122	(111,626)
6	92,532	
7	92,613	
8	92,969	
9	96,827	
10	93,037	
11	93,849	
50% B	20,203	
50% D	92,772	
45% B	20,092	
45% D	92,521	
40% B	19,543	
40% D	93,044	
35% B	24,517	
35% D	92,051	(140,425)
1 min test	85,47	

Figur C.1: Photocopy of the lab journal used for the experiment.