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ST4 - Separation by Distillation Columns

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 affection 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

1. Turn on the PC and the cooling water.
2. Make sure that the bottom and distillate tap lines are closed.
3. Fill the column with ... mL ethanol and ... mL water, and set the column to total reflux.
4. Set the temperature to 105 °C.
5. When the temperature changes substantially, or the pressure difference over the column rises quickly, set the boilers' power duty to 50%.
6. Start the time when the vapour stream starts condensing.

In case of flooding conditions, switch off the heater immediately. In any emergency situation, turn off the heater but leave the cooling water on.

3.2 Exercise 1: Time Required to Reach Steady State Condition

1. Set the reboiler power to 50 %, and wait until the column starts to give condensate.
2. Take samples from the top every 5 minutes, until 12 samples have been taken.
3. After taking sample number 12, take one sample from the bottom of the column to be used for the next exercise. Note down the temperature and pump flow rate.
4. Analyse all samples to find out how long it takes the column takes to reach steady state.

3.3 Exercise 2: Efficiency vs. Vapour Velocity

1. Set the reboiler power to 40 %.
2. Wait until the column reaches steady state. This will be at the same time as in exercise 1.
3. Take samples of 20 mL from the top and bottom, and write down the reflux rate at the time of sampling.
4. Repeat three more times with different boiler power settings.
5. Analyse the samples and calculate the vapour velocity, the efficiency of the column, and the theoretical number of stages using McCabe-Thiele.

3.4 Column Shutdown

1. Turn off the heater.
2. Let the column with contents cool down.
3. Empty the column and turn off the cooling water.
4. Turn off the rest of the equipment.

3.5 Gas Chromatography Analysis

1. Prepare the samples for the GC by mixing 500 µL of ethanol sample with 250 µL of isopropanol in a glass vial.
2. Seal the vials properly with a cap.
3. Analyse the samples using gas chromatography.

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

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

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

A Calculations

A.1 Water and ethanol mixture

The physical properties used when calculating the volumetric composition of the water-ethanol-mixture are shown in table A.1. Here Mm is the molar mass, ρ is the density, and x is the mole fraction:

Tabell A.1: caption[3]

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.

Putting equation A.1, A.3 and A.4 in to equation A.2, gives:

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

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

$$V_{EtOH} = 1596.1\,\mathrm{mL}.$$

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

$$V_{\mathrm{H_2O}} = 4203.9\,\mathrm{mL}.$$

B Example calculations

B.1 Distillate and Bottom Compositions from Pycnometers

It is desired to calculate the mole fractions of ethanol in both the distillate and bottom product, by using pycnometers, and comparing with the GC calibration results. To find this, equation A.2 can be rewritten as:

$$\begin{aligned} x_{EtOH} &= \frac{\frac{m_{EtOH}}{Mm_{EtOH}}}{\frac{m_{EtOH}}{Mm_{EtOH}} + \frac{m_{\mathrm{H_2O}}}{Mm_{\mathrm{H_2O}}}} \\ &= \frac{\frac{wt\%_{EtOH}}{Mm_{EtOH}}}{\frac{wt\%_{EtOH}}{Mm_{EtOH}} + \frac{wt\%_{\mathrm{H_2O}}}{Mm_{\mathrm{H_2O}}}} \end{aligned} \tag{B.1}$$

To calculate x_{EtOH}, the weight percentage of EtOH, $wt\%_{EtOH}$, must first be found. First the densities of the distillate and bottom product are calculated by equation B.2 and B.3, respectively:

$$\rho_{distillate} = \frac{\rho_{water} \cdot m_{distillate}}{m_{water}} = \frac{(16.0903 - 11.98170) \cdot 0.997}{16.95955 - 11.98170} = 0.8229\,\mathrm{g/cm^3} \tag{B.2}$$

$$\rho_{bottom} = \frac{\rho_{water} \cdot m_{bottom}}{m_{water}} = \frac{(16.6962 - 1.77385) \cdot 0.997}{16.75745 - 1.77385} = 0.9847\,\mathrm{g/cm^3} \tag{B.3}$$

Then the ethanol-water density-composition data at 25 °C from Perry's handbook[4], can be used to estimate the weight percentage of ethanol in the distillate and the bottom product, based on the calculated densities. The weight percentages are estimated to be about 88% for the distillate and 8% for the bottom product.

By putting these values into equation B.1, the mole fractions of ethanol are calculated to be:

$$X_{EtOH,distillate} = 0.741$$

$$X_{EtOH,bottom} = 0.033$$

These values are almost the same as the results from the GC analysis, which means that the two methods lead to approximately the same result.

B.2 Vapour Velocity

The vapour velocity is calculated using

$$v = \frac{\dot{V}_{gas}}{A}, \tag{B.4}$$

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:

$$A = \frac{\pi}{4} D^2, \tag{B.5}$$

where D is the diameter of thee column.

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

$$\dot{V}_{gas} = \frac{\dot{n}RT}{p}, \tag{B.6}$$

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

By inserting equation B.5 and B.6 into equation B.4, the vapour velocity can be calculated:

$$v = \frac{4\dot{n}RT}{\pi D^2 p}, \tag{B.7}$$

It is given that the diameter of thee column is 0.05 m, the temperature is 25 °C, and the pressure is 1 bar. Before calculating v, the molar flow needs to be found. This is found by:

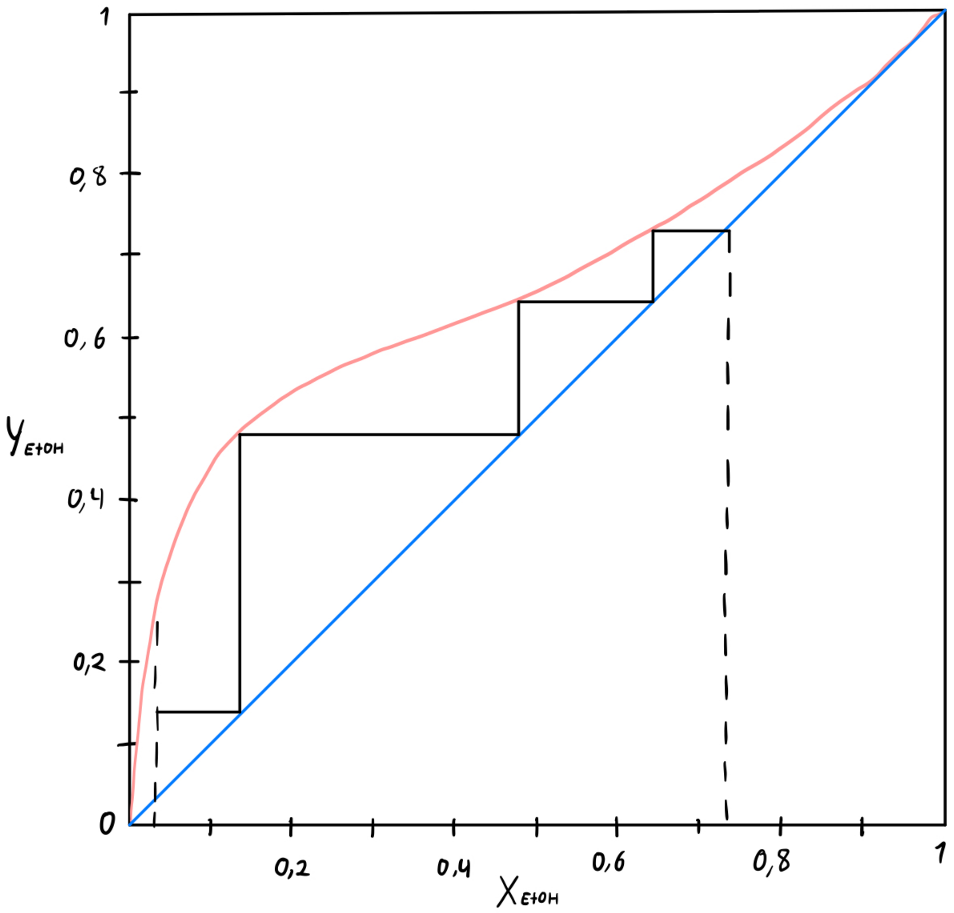
$$\begin{aligned} \dot{n} &= \frac{\dot{m}}{Mm} = \frac{\dot{V} \cdot \rho_{distillate}}{X_{EtOH} \cdot Mm_{EtOH} + (1 - X_{EtOH}) \cdot Mm_{\mathrm{H_2O}}} \\ &= \frac{53 \cdot 0.8229}{0.741 \cdot 46.07 + 0.259 \cdot 18.016} = 1.124\,\mathrm{mol\,min^{-1}} = 0.0187\,\mathrm{mol\,s^{-1}} \end{aligned} \tag{B.8}$$

Then the vapour velocity can be calculated by putting the given and calculated values into equation B.7:

$$v = \frac{4 \cdot 0.0187 \cdot 8.314 \cdot 298}{\pi \cdot 0.05^2 \cdot 10^5} = 0.24\,\mathrm{m\,s^{-1}} \tag{B.9}$$

B.3 Number of Ideal Stages Using McCabe-Thiele

Figure B.1 shows the McCabe-Thiele diagram for the mixture. Given total reflux, both the lower and upper operating line are equal to y = x. The equilibrium line was found using data from Vapor-Liquid Equilibrium Data Collection [5]. The number of ideal stages is equal to approximately 3.8.



Figur B.1: cap