Practica in Process Engineering II Distillation

Introduction

Distillation is the process of heating a liquid solution, or a liquid-vapor mixture, to derive off a vapor and then collecting and condensing this vapor. In the simplest case, the products of a distillation process are limited to an overhead distillate and a bottoms, whose compositions differ from that of the feed. Distillation is one of the oldest and most common method for chemical separation. Historically one of the most known application is the production of spirits from wine. Today many industries use distillation for separation within many categories of products: petroleum refining, petrochemicals, natural gas processing and, of course, beverages are just some examples. The purpose is typically the removal of a light component from a mixture of heavy components, or the other way around, the separation of a heavy product from a mixture of light components.

The aim of this practicum is to refresh your theoretical knowledge on distillation and to show you working distillation column in real life. One of the goals of this practicum is also to write a good report which contains physically correct explanations for the phenomena you observed. In the following sections a description of the distillation column is given, your theoretical knowledge is refreshed and the practical tasks are discussed. The final section is about the report you are expected to hand in to pass the practicum. The report is an important part of the practicum as it trains your ability to present results in a scientific way.

Description of the Distillation Column

The distillation column used in this practicum is a bubble cap column with fifteen stages fed with a liquid mixture of 60% 2-propanol and 40% 2-butanol, which is fed as a boiling liquid. Ten stages are located in the stripping section of the column and five stages are located in the rectifying section. Therefore, the feed is introduced between the 10th and 11th stage. A picture of the distillation column can be seen in figure 1. In the bottom part of the column, a part of the down-coming liquid stream is removed from the column (bottoms product), which contains more of the less volatile component of the mixture fed to the column. Heating elements are installed in the bottoms to make the liquid mixture evaporate in the whole column. From there on, the produced vapor rises and gets into contact with the liquid on the next stage. Coupled mass and heat transfer happens between the two phases and condensation/evaporation happens. This is the reason for the separation of the two compounds. The vapor leaves the top end of the column through a chimney into a total condenser, where all vapor is condensed. To efficiently control the column, the reflux ratio has to be controlled. To do this, the condensed vapor is given onto a funnel which is depicted in figure 2. The funnel is attracted by an electromagnet when switched on (drawn on the right side of the funnel in figure 2) and the liquid leaves the column through an exit pipe, giving the distillate product in this way. When the electromagnet

is switched off, the funnel moves back into its original position and the liquid is fed back to the column. Hence, the reflux ratio is controlled by switching the electromagnet on and off. The ratio between the "on" and "off" times is the reflux ratio, which can be set at a controlling element installed next to the column.

Bubble cap trays are installed inside the column, as drawn in figure 3. In the lower part of figure 3, the bubble cap is seen from the side. The vapor raises through the cap in the middle and is bubbled through the liquid on the stage. The liquid enters the bubble cap stage through a pipe coming from a tray just above the depicted bubble cap tray. The liquid then flows in a circular flow around the bubble cap in the middle (where the vapor comes out) and leaves the current tray to a lower tray through another pipe. The two pipes for the liquid streams are separated by a wall, so that no liquid can directly flow from the entering pipe to the exit pipe without undergoing extensive heat and mass transfer with the vapor phase. Understanding the principle of this bubble cap tray, one realizes that the flows in a distillation column constructed in this way are actually not counter-current but cross-flow on every stage. Therefore, you should expect some deviations between the theoretical separation capacity of a distillation column and the actual separation capacity reached in this practical setup.

The separation behavior of the column is analyzed by withdrawing samples from every stage of the column. These samples are then analyzed in a refractometer which measures the refractive index of the mixture in the sample. The refractive index can be correlated to the mass fraction of 2-propanol in the sample, which is the relation given in equation 1, where x_{prop} is the mass fraction of 2-propanol in the sample and n is the refractive index measured with the refractometer.

$$x_{prop} = (n - 1.397) / -0.0002004 \tag{1}$$

Theoretical background

In a distillation column mixtures of several components are separated by exploiting the vapor/liquidequilibrium. To do this, vapor from the lower part of the column is brought into contact with liquid from the upper part of the column. The vapor is then enriched in the more volatile components and the liquid is enriched with the less volatile components. If the vapor and liquid are in counter-current and several equilibrium stages exist in the column, one talks about rectification.

The foundation of the rectification is the mass transfer between two phases in equilibrium. In the simplest case the present components form an ideal mixture in both phases and the vapor/liquid equilibrium can be described with Raoult's law (equation 2), where y_i is the mole fraction of component *i* in the vapor phase, x_i is the mole fraction of component *i* in the liquid phase, p is the total pressure and $P_i^S(T)$ the vapor pressure of component *i*, which is of course temperature dependent.

$$y_i p = x_i P_i^S(T) \tag{2}$$

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Figure 1: Photo of the distillation column used in the practicum.



Figure 2: Schematic of the funnel used to control the reflux ratio in the column.



Figure 3: Top and side-view of a bubble cap that is used in the distillation column.



Figure 4: A schematic representation of a destillation column used to separate a binary mixture. The mass fractions indicated are for the more volatile component.

For the vapor pressure of component *i* an empirical correlation, like the Antoine equation given in equation 3, can be used. The constants A_i , B_i and C_i are given in the appendix of this document. In this equation the temperature *T* is given in [°C] and the vapor pressure P_i^S is given in [mmHg].

$$\log_{10}(P_i^S(T)) = A_i - \frac{B_i}{T + C_i}$$
(3)

To correct for non-idealities in the liquid phase, one can introduce the so-called activity coefficient γ_i , as in equation 4.

$$y_i p = x_i \gamma_i P_i(T) \tag{4}$$

There are different empirical correlations for the activity coefficients available. There is for example the commonly used van-Laar equation (equation 5) for the activity coefficient in a binary mixture. The places of A_{12} and A_{21} are exactly opposite for the other component in the mixture. The parameters A_{12} and A_{21} can be found for a lot of compounds in data collections, e.g. in [1]. For the mixture handled in this practicum, the values for these constants are given in the appendix of this document.

$$\ln(\gamma_i) = A_{12} \left(\frac{A_{21}x_2}{A_{12}x_1 + A_{21}x_2}\right)^2 \tag{5}$$

Figure 4 is a schematic representation of the distillation column, where F, D and B refer to the flow rates in the feed, the distillate and the bottoms. L_i and V_i refer to internal liquid and vapor

streams, where i is the number of the stage the respective stream is originating from. Based on the schematic, one can formulate an overall and component material balances over the column (also called the external balances, equation 6), where all mass fractions x_i refer to the lighter component of the binary mixture in the column.

$$F = D + B$$

$$Fz_F = Dx_D + Bx_B$$
(6)

Similar equations can be written for the condenser and the reboiler, see equations 7 and 8 respectively. This time, it is important to also include the heat balance and the equilibrium condition (third and fourth line of equations 7 and 8), so we can calculate the heat added in the reboiler (Q_r) and the heat removed in the condenser (Q_c) . The equilibrium relationship is given by the equations introduced before (equations 2 and 4). The symbols h_i and H_i refer to the enthalpies in the liquid and vapor phase respectively. The ratio L_0/D is commonly known as the reflux ratio R.

$$V_{1} = L_{0} + D$$

$$V_{1}y_{1} = L_{0}x_{D} + Dx_{D}$$

$$V_{1}H_{1} + Q_{c} = L_{0}h_{0} + Dh_{D}$$

$$y_{1} = f(x_{D})$$
(7)

$$L_{n} = V_{n+1} + B$$

$$L_{n}x_{n} = V_{n+1}y_{n+1} + Bx_{B}$$

$$L_{n}h_{n} = V_{n+1}H_{n+1} + Bh_{B}$$

$$y_{1} = f(x_{D})$$
(8)

This analysis can now be repeated for every stage in the rectifying and stripping section, see equations 9 and 10.

$$V_{j} = L_{j-1}$$

$$V_{j}y_{j} = L_{j-1}x_{j-1}$$

$$V_{j}H_{j} = L_{j-1}h_{j-1}$$

$$y_{j} = f(x_{j-1})$$

$$V'k + 1 = L'_{k}$$

$$V'k + 1y_{k+1} = L'_{k}x_{k}$$

$$V'k + 1H_{k+1} = L'_{k}h_{k}$$

$$y_{k+1} = f(x_{k})$$
(10)

This analysis does not hold for the feed stage, where the feed has to be included for the balances. For the sake of brevity, these balances are not given here. It can be seen from equations 9 and 10 that in this rather general formulation of the balances, the vapor and liquid flow rates differ from stage to stage. If constant molar overflow (CMO) is assumed, this is not any more

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true and the balances can be simplified. This assumption states that for every mole of liquid mixture that evaporates, one mole of vapor condenses. By consequence, it is also assumed that both components have the same heat of vaporisation, which is a reasonable assumption only for similar compounds. The CMO assumption allows us to assume the flow rates of the liquid and vapor to be constant within one section of the column (rectifying section: V and L const.; stripping section: L' and V' const.). However, neither L' and L, nor V' and V are the same (because of the feed).

Using this knowledge, one can derive the working lines for both sections of the column quite easily and they are given here without further derivation, see equations 11 and 12.

$$y = \frac{L}{V}x + \left(1 - \frac{L}{V}\right)x_D\tag{11}$$

$$y = \frac{L'}{V'}x + \left(1 - \frac{L'}{V'}\right)x_B \tag{12}$$

Another useful quantity is the feed quality q, which can defined as given in equation 13. A value of q = 1 means that the feed is added as a boiling liquid, q = 0 means the feed is a saturated vapor, q < 0 means the feed is a superheated vapor and q > 1 means the feed is a supercooled liquid.

$$\frac{V-V'}{F} = q - 1 \tag{13}$$

By drawing the working lines for both sections, knowing the x_B and x_D and the feed composition, one can draw the **McCabe-Thiele diagram** for the given distillation column. This gives you a graphical representation of the theoretical number of stages in the distillation column. This number can then be compared to the real number of stages and a statement can be made about the stage efficiency in the column. Have a look at Hyper-TVT[2] if additional theoretical ressources are required.

Experimental Tasks

The start-up of the column is done by the assistent some time before the practicum, so that the column has reached the operational steady state when the students arrive for the practicum. The general task is to operate the distillation column at two different reflux ratios R (R = 2.67 and R = 5) and characterize the operation of it. To characterize the operation of the distillation column, one has to do the following:

- Draw samples from every stage, the bottoms, the feed and the distillate.
- Measure the refractive index for every sample with a refractometer. Make sure the refractometer is exactly at 20C because the refractive index is temperature dependent.

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- Measure the volumetric flow rate of the feed, the distillate and the bottoms.
- Read and write down all the relevant values for an energy balance from the control element next to the column.

After everything is done at R = 2.67, the assistant will show you how to switch the column to a reflux ratio of R = 5. Unfortunately, it takes about 30 minutes to reach the steady state after the reflux ratio is changed. This time can be used to analyze the samples taken for the lower reflux ratio. After the second round of sampling the assistant has to be informed and a quick check is done if all the relevant values were written down. The practicum is finished after this step and the report writing can begin. For instructions regarding the report, see next section.

Report

A report has to be written containing all the important information of the experiments carried out. The report should include, but is not limited to, the following items:

- title page: the title page includes a title (obviously), your names, your email adresses, the date you handed the report in and a small abstract.
- introduction: a small introduction that explains what experiment you are doing and what insight you want to gain.
- theory section: the theory section includes all the equations you are going to use to interpret your results. Derivations **do not** have to be included, but you should shortly state the principle behind the equations used. If assumptions have to be made for an equation to be valid, they have to be stated.
- experimental part which includes **what** you did, **why** you did it and **how** you did it.
- results and discussion: in this part your results are included. Your measurement results have to be explicitly given, so that any calculations are reproducible. The following plots and tables **are the minimum required**:
 - 1. The experimental flow rates have to be compared to the calculated flow rates using the overall mass balance.
 - 2. A calculation of the energy loss over the whole column using an energy balance.
 - 3. The x-y diagram for the ideal and real (activity coefficient corrected) case of the mixture.
 - 4. The corresponding T-xy diagram
 - 5. The weight fraction of 2-propanol versus stage number.
 - 6. Temperature versus stage number.
 - 7. McCabe-Thiele diagrams for the ideal and real case.
 - 8. A table with all the data measured in the practicum, so that your calculations can be verified.

This part also includes the discussion of your results. In the discussion you state if the results you obtained were expected. If they were not expected, give explanations why they are not what you expect. This section is the most important section of your report because it gives the indication if you understood what you were doing. All the figures you are implementing in the report have to be commented (**what** can be seen and **why** do you think it is important to show?). Reports that give no or thermodynamically impossible explanations for the observed phenomena will be rejected or have to be corrected.

You have three weeks time to hand in a report that meets these standards, which includes possible corrections you have to make. Therefore, it is recommended to hand in the first version of the report earlier, so that you have time to correct possible mistakes. The time the assistant takes to correct your report is **not** included in the three weeks. The report can be handed in either digitally or as hard copy directly at the assistant's office.

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Appendix

Constants for the van Laar equation (2-Propanol is the component for which equation 5 holds), taken from [1]:

 $\begin{array}{l} A_{12}=0.0730\\ A_{21}=0.0785\\ \text{Constants for the Antoine equation, equation 3, taken from [1] as well:}\\ \textit{2-Propanol:}\\ A=8.87829\\ B=2010.330\\ C=252.636 \end{array}$

2-Butanol: A = 7.47429 B = 1314.188C = 186.500

References

- [1] Gmehling, J.; Onken, U.: "Vapor-Liquid Equilibrium Data Collection", Chemistry Data Series, DECHEMA.
- [2] www.hyper-tvt.ethz.ch