

LABORATORY OF SEPARATION PROCESSES

**Work No. 9**

Differential distillation of binary mixtures

**IN A NUTSHELL**

Distillation is one of the ways to separate components from a homogeneous liquid mixture. It is a diffusion separation process based on the different volatilities of the separated components, with the tendency for more volatile component to pass into the distillate. Differential distillation is a batch process that is simpler to implement compared to continuous distillations. Therefore, it can also be encountered in everyday life, with the most typical application being the traditional two-stage (or multi-stage) fruit spirit distillation. To better understand differential distillation, let's imagine the process over time (Fig. 1). The feed with molar amount and composition is poured into the boiler and heated until the temperature , at which the mixture begins to boil, is reached. At this temperature, vapors that are in equilibrium with the boiling mixture are formed. Their composition can be read from the condensation curve of the *t-x,y*  diagram. As we see, there is a higher proportion of the more volatile component in the vapor than in the feed. The formed vapor is led to the condenser, where it fully condenses and leaves the apparatus as the first drop of distillate. This drop has the same composition as the vapor from which it formed, hence. In the boiler, a mixture remains, now we can also call it residue,, which has precisely that much less of the more volatile component as has left in the first drop of distillate. This means that the composition of the residue will move a bit to the left along the boiling curve of the *t-x,y* diagram. At the same time, a slight increase in distillation temperature is observed. Such changes over a short period are technically called differential changes, which is where the name differential distillation comes from. The original equilibrium is disturbed, and the vapors leaving in the next moment will have a lower content of the more volatile component , corresponding to the new equilibrium state with the boiling residue . In differential distillation, therefore, the equilibrium is constantly disrupted, with the content of the more volatile component in the distillate and residue continuously decreasing. If during the entire distillation we collect the distillate into one container, its composition () is given by the average value of the composition of the first () and the last drop of distillate (). The amount and composition of the final distillate can only be regulated by the amount of the distilled mixture. Therefore, the distillation is ended when the desired composition of the final distillate is reached, leaving the residue in the boiler with molar amount and composition (Fig. 2).

|  |  |
| --- | --- |
| Obrázok, na ktorom je rad, diagram, náčrt, vývoj  Automaticky generovaný popis |  |
| *Fig. 1 t-x,y diagram of binary mixture* | *Fig. 2 Flow diagram of differential distillation with representation of initial and final state.*  |

If we want to achieve higher purity of the distillate, the distillation can be repeated in several stages, where the obtained distillate is used as feed in the subsequent distillation stage. Now we understand the origin of the name differential distillation and remember that in this process, the boiling temperature, composition, as well as the amount of distillate and residue, change differentially over time.

# Theory

In order to describe this type of distillation in terms of mass balance, we can use three equations. For differential distillation, the overall mass balance as well as the balance for the more volatile component are given by:

|  |  |  |
| --- | --- | --- |
|  |  | (1) |
|  |  | (2) |

where is molar amount of feed, and are molar amounts of distillate and residue. The mole fractions in the equilibrium (2) represent the proportion of the more volatile component in the feed, distillate and residue.

By calculating the more volatile component during a differential time interval, we can derive Rayleigh equation, which expresses the dependence between the molar amount of liquid at the beginning () and at the end () of the process and its composition.

|  |  |  |
| --- | --- | --- |
|  |  | (3) |

In calculations, the assumption is made that the boiling liquid in the boiler is in instantaneous equilibrium with the vapor leaving the condenser.

|  |  |  |
| --- | --- | --- |
|  |  | (4) |

Equilibrium can be expressed using the appropriate equilibrium equations or using the experimental data.

In addition to the three material balance equations mentioned, we can also describe the enthalpy balance for this type of distillation in the form:

|  |  |  |
| --- | --- | --- |
|  |  | (5) |

Where the parameters with the indexes *F*, *D* and *W* represent the enthalpy of the feed, distillate vapor or residue, respectively, is total energy introduced to the system necessary to perform the distillation, is the energy lost (represents mainly the heating of the apparatus and the heat loss by flow and radiation to the surroundings during the distillation process).

In case we choose the liquid state, atmospheric pressure, and the temperature of the feed as the reference state in equation (5), the first term on the left side of equation (5) will be zero.

Then, equation (5) states that the total energy introduced into the system is divided into three parts: the enthalpy of the outgoing distillate or residue and the energy lost from the system to the surroundings.

The thermal efficiency of processes is generally defined by the equation:

|  |  |  |
| --- | --- | --- |
|  |  | (6) |

Where is the amount of energy utilized in the process and is the total amount of energy introduced to the system required to perform the process.

In differential distillation, we consider as useful energy the portion of the energy that is used to heat the feed from the initial temperature to the distillation temperature and to vaporize the corresponding amount of distillate. On a laboratory scale, the total amount of energy, when using electric heating, is measured with an electric meter. Then, equation (6) takes the form:

|  |  |  |
| --- | --- | --- |
|  |  | (7) |

where is molar heat capacity and is molar enthalpy of vaporization.

The distillation temperature in the case of differential distillation is not constant, but, assuming a linear increase, it can be calculated as the average value of the distillation temperature at the beginning () and end of the distillation ().

|  |  |  |
| --- | --- | --- |
|  |  | (8) |

# Objectives of the work

1. Process a given molar amount of a binary mixture with known composition to differential distillation at atmospheric pressure. Calculate both molar amount and the composition of the distillate and the residue, then compare the calculated values with the measured data.
2. Calculate the degree of utilization of the heat introduced for distillation from the measured data.

# Assignment of the work

Perform a two-step differential distillation of a binary methanol-ethanol mixture with the of 55 moles of feed. The first stage of the distillation is conducted at performance of 1400 W so that 65 % of the stock is distilled off into the distillate. The distillate from the first distillation step is used as feed for the second distillation step. The second stage of distillation is conducted at performance of 1000 W so that 50 % of the distillate from the first stage passes into the distillate. Compare the measured and calculated composition of the distillate and the residue for the two stages of distillation. From the measured data, calculate the degree of heat utilization in both distillation stages.

# equipment description

The experiment is performed in a laboratory distillation apparatus, which is schematically shown in Fig. 3. In the schematic diagram, all devices are duplicated.



Fig. 3 Schematic diagram of the distillation apparatus for differential distillation of binary mixture.

1 – boiler (distillation tank), 1a – cooling coil, 1b – cooling water outlet, 1c – filling valve, 1d – vapor outlet, 1e – safety pressure valve, 1f – thermometer T1 (distillation temperature), 1g – cooling water inlet, 1h – distillate residue outlet valve, 2 – induction heater, 3 – condenser (tube-in-tube heat exchanger), 3a – condenser cooling water outlet, 3b – condenser cooling water inlet, 4 – thermometer T2 (distillation temperature), 5 – distilled outlet from condenser, 6 – distillate sampling, 7 – distillate template with magnetic stirrer, 8 – magnetic stirrer, 9 – digital scales, 10 – control panel, 10a – main swith, 10b – wattmeter, 10c – distillate temperature display (thermometer T1), 10d – distillate temperature display (thermometer T2), 11a – condenser cooling water valve, 11b – cooling water valve to the boiler cooling coil, 12 – at the bottom of the apparatus there is a template for the distillate residue.

# working procedure

## Safety precautions

1. During work, especially when handling samples, it is important to proceed with caution because the substances being used are highly flammable class 1 materials, and methanol is a dangerous poison!

## preparation fot the measurement

Note: Write all values of the parameters given in brackets in Table 1 for the first stage and Table 2 for the second stage.

1. Firstly, we will inspect the equipment and check it for completeness. Then, we will prepare the digital refractometer for measurement.
2. Calculation of the volume and weight of feed for distillation:

Take a sample of the feed and measure its index of refraction. From the calibration diagram in the file we determine the mole fraction of the more volatile component in the feed. Next, the temperature of the feed needs to be measured and from these two values, the molar volume of the feed needs to be determined using the information from the file. Using the known molar volume, the molar amount of the feed can be easily recalculated into the volume of feed to be poured into the boiler for distillation.

|  |  |  |
| --- | --- | --- |
|  |  | (9) |

The quantity of feed needed can be expressed in mass.

|  |  |  |
| --- | --- | --- |
|  |  | (10) |

where and are molar masses of the more volatile and less volatile component.

1. Calculation of the differential distillation according to the work assignment:

Molar amount of distillate is determined as a percentage of the molar amount of feed. Using the total material balance of distillation (1), we can easily evaluate the molar amount of residue. Based on this data, we can solve equation (3) whose left side, , we can already quantify. However, on the right side of the equation (3) is the unknown limit of the integral. To obtain the value, we proceed with the next calculation as follows: integral on the right side of the equation (3) is divided into two integrals.

|  |  |  |
| --- | --- | --- |
|  |  | (11) |

The value of the first integral for the binary methanol-ethanol mixture can be found in the Table of Integrals attached, for the composition . The value of the second integral is calculated from equation (11), where the value of the first integral is subtracted from the left side of the equation:

|  |  |  |
| --- | --- | --- |
|  |  | (12) |

The unknown value of the composition of residue is determined retrospectively using the Table of Integrals for the calculated value of the integral from equation (12).

1. Then, from the material balance for the more volatile component (2), the mole fraction is calculated.
2. The mass of the resulting distillate is calculated as followed:

|  |  |  |
| --- | --- | --- |
|  |  | (13) |

1. The accuracy of the calculation will be reviewed by your supervisor.

## MEranie

Note: Write all the values of the parameters given in brackets in Table 3 for the first stage and Table 4 for the second stage.

1. With the main switch [10a] switch on the supply of electric power to the laboratory apparatus. Turn on the scales [9] and press the ON/OFF button on the induction boiler [2].
2. Using a measuring cylinder, prepare the calculated volume of feed. Weigh the mass of feed () using an empty beaker.
3. Through the filling valve [1c] pour the required amount of feed into the boiler. Close the valve!
4. Place the template with the magnetic stirrer [7] on the scales, reset them by pressing the TAR button. Record the initial state of *Wh* () on the wattmeter [10b], note the initial temperature of the feed () on the display [10c] , switch on the induction heating of the boiler [2] by pressing the MODE button and use the rotary converter to set the desired heating performance. Through the valve [11a], the condenser [3] is fed with cooling water from the tap (at the appropriate flow rate). Observe the rate of temperature rise of feed in the boiler. Note the boiling temperature () in the boiler at the moment when the first drop of distillate appears.
5. During distillation, observe the increase in distillate weight as well as the distillation temperature in the boiler. Switch on the magnetic stirrer [8] to ensure homogenization of the distillate. After distilling every 200 g of distillate, take a sample using a sample syringe [6] to determine the composition of the distillate and note the distillation temperature () in the boiler. Samples are collected by first washing the sample port and then collecting approximately 0,5 ml of the distillate to determine the index of refraction. The refractive index is converted to the mole fraction of the more volatile component (). The actual weight of the distillate is calculated in moles using the equation (13).
6. When the calculated (final) mass of distillate () has been distilled, turn off the induction heating, note down the final value of the distillation temperature () as well as the final value on the wattmeter (). Replace beaker with distillate with an empty beaker to capture the output from the condenser. Take the last sample of distillate from and determine the mole fraction of the more volatile component () .
7. Using the valve [11b], let the cooling water into the cooling coil of the boiler, wait until the temperature in the boiler drops to 45°C (45°F). Open valve [1h] to empty the residue into the pre-weighed (or zeroed) residue beaker [12]. Into the same vessel add the contents of the beaker into which we captured the output from the condenser. Measure the weight of residue () and take a sample of residue in which the mole fraction of the more volatile component () is determined. Close the outlet valve [1h].
8. If the subject of the assignment is a two-stage distillation, the distillate obtained in the first stage is poured as the feed into the boiler. When calculating the amount of the final distillate from the second stage, we assume the real, measured, values of distillate from the first stage (final distillate from the first stage = feed for the second stage). The calculation and measurement are the same as for single-stage distillation, the only difference being that in the second stage sample is collected from the homogenized distillate after it is distilled every 100 g.

**END OF MEASUREMENT**

Pour the distillate and the residue back into the container for the feed. Stop the flow of cooling water and switch off the laboratory apparatus with the main switch.

**YOU CAN SEE THE DESCRIPTION OF THE DEVICE AS WELL AS THE WORK PROCEDURE IN THE VIDEO:**

<https://www.youtube.com/watch?v=hLhSKn7nUWU&list=PL81QAQg818vjDK7pm9WO6tW36sdBpPGYa&index=2>



# QUESTIONS - WHAT THE TEACHER MAY ASK YOU BEFORE THE EXPERIMENt

* Describe the different parts of the experimental apparatus.
* Explain what you will measure, how and why.

# MEASUREMENT DATA PROCESSING

1. Make sure the total mass balance is correct.

|  |  |  |
| --- | --- | --- |
|  |  | (14) |

1. Determine the relative deviation of the measured from the calculated values of the mole fractions of the final distillate for both the first and the second stage of distillation.
2. Next, determine the amount of useful energy () used for distillation (numerator of the equation (7)). To do this, the initial temperature of the feedstock () and the average temperature during distillation need to be determined. The molar heat capacity of the feed is calculated additionally according to the composition of the feed.

|  |  |  |
| --- | --- | --- |
|  |  | (15) |

where the subscripts *A* and *B* represent the more volatile and less volatile components, respectively.

The heat capacities of the components are determined at the specifying temperature:

|  |  |  |
| --- | --- | --- |
|  |   | (16) |

The molar evaporative enthalpy of the components is determined for the middle distillation temperature and the heat of vaporization of the distillate is calculated additively according to the composition of the distillate.

|  |  |  |
| --- | --- | --- |
|  |  | (17) |

1. The amount of total energy input to the distillation in a given stage is calculated as the difference between the final and initial state of the wattmeter.
2. Based on this, the heat recovery rate of distillation can be calculated according to equation (7).
3. From the measured data, plot a dependence graph .

# TABles

Tab. 1 Data obtained before measurement for the first stage

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *t*F =  |   | °C | *m*F = |   | g |
| *IL*F = |   |   | *x*W = |   |   |
| *x*F = |   |   | *x*D = |   |   |
| *V*M,F = |   | l mol-1 | *m*D = |   | g |
| *V*F = |   | l |  |  |  |

Tab. 2 Data obtained before measurement for the second stage

|  |  |  |
| --- | --- | --- |
| *x*W = |   |   |
| *x*D = |   |   |
| *t*D = |   | °C |
| *m*D = |   | g |

Tab. 3 Record of measured data from the first stage of distillation.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| No. measuremtnt | *m*D (g) | *n*D (mol) | *t*d (°C) | *IL*D | *x*D |
| 1 |  |  |  |  |  |
| 2 |  |  |  |  |  |
| 3 |  |  |  |  |  |
| 4 |  |  |  |  |  |
| 5 |  |  |  |  |  |
| 6 |  |  |  |  |  |
| 7 |  |  |  |  |  |
| 8 |  |  |  |  |  |
| 9 |  |  |  |  |  |
| 10 |  |  |  |  |  |
| *m*F = |  | g | *x*D,end = |   |   |
| *t*F,in = |   | °C | *m*D,end = |  | g |
| *Ein* = |   | kWh | *E*end = |   | kWh |
| *t*d,in = |   | °C | *x*W,end = |   |   |
| *t*d,end = |   | °C | *m*w,end = |  | g |

Tab. 4 Record of measured data from the second stage of distillation.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| No. measuremtnt | *m*D (g) | *n*D (mol) | *t*d (°C) | *IL*D | *x*D |
| 1 |  |  |  |  |  |
| 2 |  |  |  |  |  |
| 3 |  |  |  |  |  |
| 4 |  |  |  |  |  |
| 5 |  |  |  |  |  |
| 6 |  |  |  |  |  |
| 7 |  |  |  |  |  |
| 8 |  |  |  |  |  |
| 9 |  |  |  |  |  |
| 10 |  |  |  |  |  |
| *m*F = |  | g | *x*D,end = |   |   |
| *t*F,in = |   | °C | *m*D,end = |  | g |
| *Ein* = |   | kWh | *E*end = |   | kWh |
| *t*d,in = |   | °C | *x*W,end = |   |   |
| *t*d,end = |   | °C | *m*w,end = |  | g |

Tab. 5 Results of measurement

|  |  |
| --- | --- |
| I. stage of distillation | II. stage of distillation |
| *Q*tot = |   | kJ | *Q*tot = |   | kJ |
| *Q*Useful = |   | kJ | *Q*Useful = |   | kJ |
| *η*T = |   | % | *η*T = |   | % |
| *δx*W = |   | % | *δx*W = |   | % |
| *δx*D = |   | % | *δx*D = |   | % |

# attachements







Table for calculating the integral

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| *xi* | *I* | *xi* | *I* | *xi* | *I* | *xi* | *I* |
| 0,02 | 0,91927 | 0,26 | 7,82567 | 0,51 | 6,74925 | 0,76 | 9,04641 |
| 0,03 | 1,44476 | 0,27 | 4,90920 | 0,52 | 6,82654 | 0,77 | 9,16835 |
| 0,04 | 1,82274 | 0,28 | 4,99149 | 0,53 | 6,90439 | 0,78 | 9,29465 |
| 0,05 | 2,12209 | 0,29 | 5,07265 | 0,54 | 6,98286 | 0,79 | 9,42573 |
| 0,06 | 2,37238 | 0,3 | 5,15282 | 0,55 | 7,06203 | 0,8 | 9,56209 |
| 0,07 | 2,58907 | 0,31 | 5,23209 | 0,56 | 7,14195 | 0,81 | 9,70429 |
| 0,08 | 2,78130 | 0,32 | 5,31057 | 0,57 | 7,22270 | 0,82 | 9,85299 |
| 0,09 | 2,95496 | 0,33 | 5,38834 | 0,58 | 7,30436 | 0,83 | 10,00898 |
| 0,1 | 3,11403 | 0,34 | 5,46550 | 0,59 | 7,38699 | 0,84 | 10,17317 |
| 0,11 | 3,26135 | 0,35 | 5,54212 | 0,6 | 7,47067 | 0,85 | 10,34665 |
| 0,12 | 3,39902 | 0,36 | 5,61829 | 0,61 | 7,55550 | 0,86 | 10,53073 |
| 0,13 | 3,52864 | 0,37 | 5,69406 | 0,62 | 7,64156 | 0,87 | 10,72702 |
| 0,14 | 3,65144 | 0,38 | 5,76952 | 0,63 | 7,72894 | 0,88 | 10,93753 |
| 0,15 | 3,76840 | 0,39 | 5,84473 | 0,64 | 7,81776 | 0,89 | 11,16477 |
| 0,16 | 3,88033 | 0,4 | 5,91974 | 0,65 | 7,90812 | 0,9 | 11,41198 |
| 0,17 | 3,98787 | 0,41 | 5,99463 | 0,66 | 8,00013 | 0,91 | 11,68346 |
| 0,18 | 4,09156 | 0,42 | 6,06946 | 0,67 | 8,09392 | 0,92 | 11,98499 |
| 0,19 | 4,19186 | 0,43 | 6,14427 | 0,68 | 8,18964 | 0,93 | 12,32474 |
| 0,2 | 4,28915 | 0,44 | 6,21913 | 0,69 | 8,28743 | 0,94 | 12,71472 |
| 0,21 | 4,38377 | 0,45 | 6,29410 | 0,7 | 8,38749 | 0,95 | 13,17365 |
| 0,22 | 4,47600 | 0,46 | 6,36923 | 0,71 | 8,49000 | 0,96 | 13,73319 |
| 0,23 | 4,56610 | 0,47 | 6,44457 | 0,72 | 8,59512 | 0,97 | 14,45386 |
| 0,24 | 4,65429 | 0,48 | 6,52019 | 0,73 | 8,70307 | 0,98 | 15,47672 |
| 0,25 | 4,74075 | 0,49 | 6,59614 | 0,74 | 8,81408 | 0,99 | 17,30594 |
|  |   | 0,5 | 6,67248 | 0,75 | 8,92843 |   |  |

## INSTRUCTIONS FOR USE OF DIGITAL REFRACTOMETER KRÜSS DR301-95

1. Connect the device to the power supply.
2. Press the ON/OFF button.
3. Open the lid and clean the prism (if necessary).
4. Drip about 3-4 drops onto the prism so that the entire surface of the prism is covered with liquid, be careful of bubbles.
5. Close the lid.
6. Press the READ/ENTER button.
7. The index of refraction will appear on the display.
8. Clean and dry the prism with a cotton stick.
9. The instrument is ready for further measurements.
10. When finished, turn off the refractometer with the ON/OFF button and disconnect the instrument from the power supply.