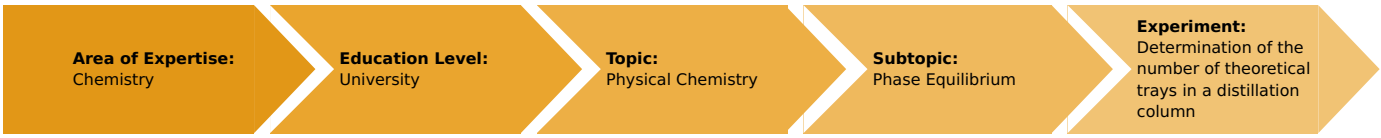
(Item No.: P3031501)

Curricular Relevance



Difficulty	Preparation Time	Execution Time	Recommended Group Size
Intermediate	10 Minutes	20 Minutes	2 Students

Additional Requirements:

- Precision balance, 620 g / 0.001 g

Experiment Variations:

Keywords:

Bubble tray column, Rectification, Raoult’s law, Henry’s law, Dalton’s law, Boiling point diagram, Reflux ratio

Task and equipment

Introduction

Principle
Fractionating distillations with columns are widelyused in the chemical industry for example in oil refinery or liquefied air separation. This important method is visualised in this model distillation plant using transparent columns. The number of theoretical trays defines the separation power of a rectification (fractionating) column. This value is numerically or graphically obtained from the measured equilibrium composition of a binary mixture in the distillation flask and in the domed glass head of the distillation apparatus.

Safety instructions

***n*-Heptane**
H225: Highly flammable liquid and vapour.
H304: May be fatal if swallowed and enters airways.
H410: Very toxic to aquatic life with long-lasting effects.
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P273: Avoid release to the environment.

Methylcyclohexane
H225: Highly flammable liquid and vapour.
H304: May be fatal if swallowed and enters airways.
H411: Toxic to aquatic life with long-lasting effects.
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P261: Avoid breathing dust/fumes/gas/mist/vapours/spray.

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Equipment

Position No.	Material	Order No.	Quantity
1	Set rectification plant, 230 V	35918-88	1
2	Abbe refractometer	35912-00	1
3	Data acquisitation set for set rectification plant, 230 V	35918-50	1
4	Immersion thermostat Alpha A, 230 V	08493-93	1
5	Stop clock, demo.; diam. 13 cm	03075-00	1
6	Bath for thermostat, makrolon	08487-02	1
7	External circulation set f. thermostat Alpha A	08493-02	1
8	HEPTANE, NORMAL 1000 ML	31366-70	1
9	Methylcyclohexane 1 l	31566-70	3
10	Funnel, glass, top dia.150 mm	34461-00	1
11	Graduated cylinder 1000 ml	36632-00	1
12	Boiling beads, 200 g	36937-20	1
13	Pasteur pipettes, 250 pcs	36590-00	1
14	Water, distilled 5 l	31246-81	2
15	Snap-cap vials,d=30mm,h=50mm,10p.	33624-03	2
16	Rubber caps, 10 pcs	39275-03	1
17	Rubber tubing, i.d. 6 mm	39282-00	4

Task

1. Determine the refractive indices of 10 mixtures of methyl cyclohexane and n-heptane to record a cali-bration curve.
2. Determine the composition of the condensate and the number of theoretical trays in the column for a throughput of 500 and 1000 ml/h.

Set-up and procedure

Set-up

Recording the calibration curve:

- Connect the refractometer to the immersion thermostat and temperature equilibrate it to 25 °C.
- Prepare the mixtures 10 mixtures of methyl cyclohexane and n-heptane with substance ratios (mole fractions) from 0 to 1 and with step width of approximately 0.1 as listed in Table 1 and immediately measure the refractive indices.

Plot the refractive indices against their mole fractions. The respective compositions of the mixtures can be graphically or numerically determined from the slope of the regression line (Fig. 1). Do not discard the mixtures; pour all of them into the distillation flask.

Table 1: Mixtures for the calibration curve

No.	n-Heptane/g	Methylcyclohexane/g	Mole fraction x of n-heptane	Mole fraction x of Methylcyclohexane
1	15.000	0.000	1	0
2	13.302	1.664	0.88679	0.11321
3	11.653	3.280	0.77685	0.22315
4	10.403	4.505	0.69351	0.30649
5	8.665	6.208	0.57764	0.42236
6	6.980	7.858	0.46533	0.53467
7	5.346	9.459	0.35643	0.64357
8	3.762	11.012	0.25079	0.74921
9	2.681	12.071	0.17870	0.82130
10	1.323	13.402	0.08817	0.91183
11	0.000	15.000	0	1

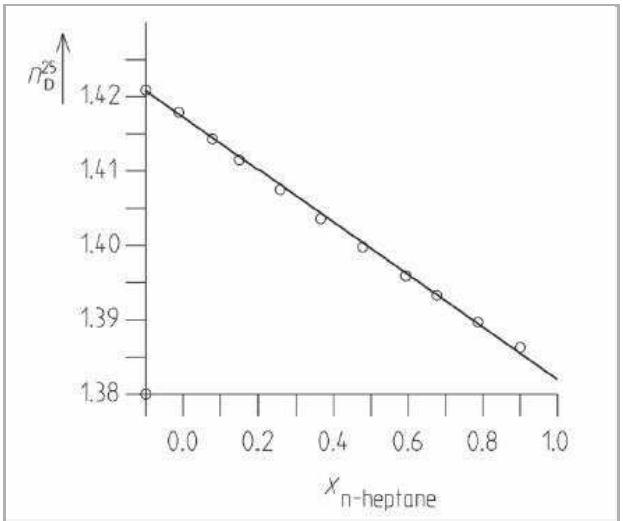

Fig. 1: Calibration curve

Procedure

Performing the measurements:

- Set up the experiment as shown in Figs. 2 and 3.
- Add further quantities of methyl cyclohexane and n-heptane to the combined mixtures in the distillation flask, so that 750 ml of n-heptane and 3000 ml of methyl cyclohexane are present in the flask. Put in a few boiling beads.
- Adjust the glass tube for the recirculation of condensate from the separatory funnel in such a manner that it ends at least 5 cm below the level of the liquid in the flask, so that vapour cannot flow up through it.
- Check the correctness and tightness of the apparatus, turn on the cooling water, and set the steam splitter to reflux.
- Set the heating hood to III and the power regulator to 8. At the onset of condensation in the reflux condenser, turn the power regulator setting down to 3.5.
- After two to three hours of distillation under total reflux, switch the steam splitter over to withdrawal and collect the distillate in the separatory funnel. Use the stop watch to determine the time required for 10 ml of condensate to collect and convert this to ml/h. The value should lie between 400 and 600 ml/h. If readjustment is necessary, wait for 30 minutes at total reflux before taking the next sample.
- When the desired throughput has been achieved, switch back to total reflux for 30 minutes until thermal equilibrium has again established. Subsequent to this, begin taking samples of the condensate.

Fig. 2: Set-up.

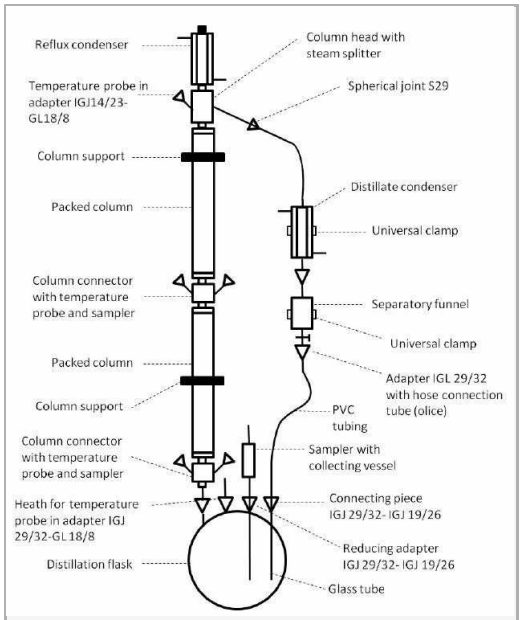

Fig. 3: Distillation apparatus

Results and evaluation

Results

The results for an exemplary measurement are presented in Table 2.
The number of theoretical trays, i.e. the separation power, decreases with increasing distillation rate. If one increases the distillation rate even more, the column becomes ‘flooded’ and does not separate at all.

Table 2: Measuring results

Measurement No.	1	2
Distillation rate (ml/h)	500	1200
x_0 (sump)	0.213	0.213
y_0 (head)	0.410	0.299
Theoretical trays n	14	7

Evaluation

Rectification is a distillation process in which, for the purpose of an improved separation, part of the condensate flows back down against the vapour and so participates in substance and heat exchange with the vapour. The mixture to be separated is heated in an evaporating vessel until it begins to boil. During boiling, the temperature continually increases because the composition of the mixture changes. A temperature gradient is formed in the column. This gradient ranges from a temperature $T_{0,A}$ below the boiling point of the substance with the highest boiling point A in the evaporating vessel up to the boiling point temperature $T_{0,B}$ of B at the head of the column. On evaporating the liquid, a vapour is formed which is enriched with the more volatile substance B. This vapour is then partially condensed on the the first col-umn tray, as this is at a lower temperature. This liberates condensation enthalpy, which heats the condensate present there. New vapour is evolved, which is again enriched with B and flows to the second tray, on which the same procedure is repeated. An exchange of energy (condensation enthalpy, enthalpy of vaporization) takes place at each tray and, alongside this, an exchange of substances. We are viewing the behaviour under the assumptions that we have „ideal trays“ and „total refluxing“, whereby an ideal tray is to be understood to be one at which the backflow of liquid is in equilibrium with the rising vapour. With total refluxing, no distillate is removed from the top of the column. All condensate returns back down the column.

For the partial pressure p_A and p_B of two components A and B in the vapour space above a liquid binary mixture and with ideal behaviour, the following is valid according to Raoult’s law:

$$p_A = P_A \cdot x_A \, p_B = P_B \cdot x_B \tag{1}$$

where p_A and p_B are the vapour pressures of the pure components, and x_A and x_B the mole fractions in the liquid phase. For a binary mixture the following is valid:

$$x_B = 1 - x_A \tag{2}$$

and the ratio of the partial pressures in the vapour space can be formulated as:

$$\frac{p_A}{p_B} = \frac{P_A}{P_B} \cdot \frac{x_A}{1 - x_A} \tag{3}$$

According to Dalton’s law, the partial pressures p_A and p_B with the total pressure p are linked over the mole fractions y_A and y_B of the two components in the gas phase:

$$p_A = p \cdot y_A \tag{4.1}$$

$$p_B = p \cdot y_B = p(1 - y_A) \tag{4.2}$$

By substituting in (3) the following is obtained:

$$\frac{y_A}{1 - y_A} = \frac{P_A}{P_B} \cdot \frac{x_A}{1 - x_A} \tag{5}$$

If no indices are given, x and y refer to the more volatile components. For the relationship of the vapour pressures of the pure components, the relative volatility is used:

$$\alpha = \frac{P_A}{P_B} \tag{6}$$

Equation (5) now becomes

$$\frac{y_A}{1 - y_A} = \alpha \cdot \frac{x_A}{1 - x_A} \tag{7}$$

and after rearranging

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$$y = \frac{\alpha \cdot x}{1 + (\alpha - 1) \cdot x} \quad (8)$$

This equation can be used to construct an equilibrium diagram (mole fraction y of the more volatile component in the gas phase against the mole fraction x in the liquid phase; Fig. 4).

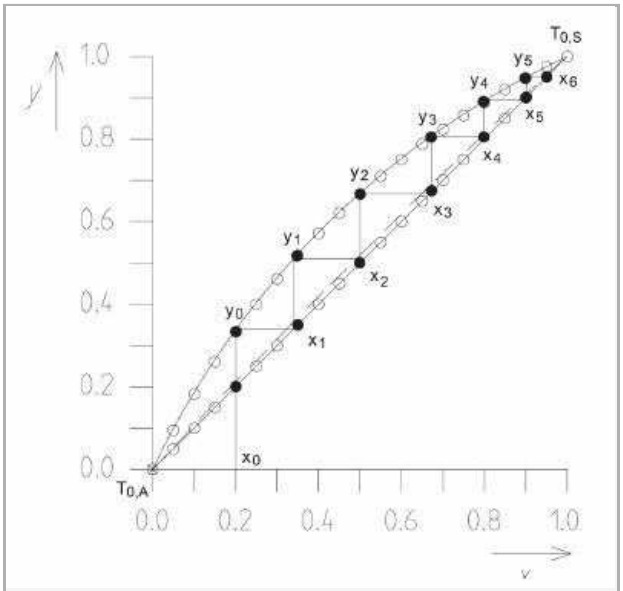

Fig. 4: Equilibrium diagram

From the isobaric equilibrium curve we can read off the exchange of substance at the individual trays. The initial mixture contains x_0 of B. On boiling, a vapour with y_0 of B is formed. This vapour is completely condensed, and no change in the composition is caused. In the diagram we reach the bisector of the angle. The condensate is again vaporized and the composition is now y_1 . We draw in a horizontal line for each condensation, and a vertical line for each vaporization, and so obtain a series of steps.

For α = 1, a 45° line is obtained. Under these conditions distillative separation of the mixture is not possible. If α > 1, curves are obtained. The upper curve in Fig. 4 corresponds to a value of α = 2. If one proceeds on the assumption that the more volatile component in the liquid mixture has a mole fraction of 0.2, one can read off the composition of the vapour by moving from the 45° line perpendicularly upwards to the equilibrium curve (y_B = 0.33). When this vapour is recondensed, move parallel to the abscissa until the 45° line is intersected. The component with the mole fraction 0.33 (complete condensation) is present in the condensate. For renewed vaporisation and condensation, a value of 0.48 is obtained, etc. Each step corresponds to a distillation procedure or a tray in an ideal bubble tray column. The greater the reflux ratio, i.e. the greater the amount of condensate which can flow back through the column, the better the separation effect. The separation power in a technical column is expressed by its number of theoretical trays. It is defined as the number of individual distillation procedures required to achieve the same enrichment of the more volatile component in the test mixture as by rectification with the column to be investigated.

The calculation of the number of theoretical trays can be performed using equation (8).

A vapour of concentration y_0 is obtained when a mixture x0 vaporises. If the condensation is complete, the new liquid phase has the same concentration, $x_1 = y_0$. After n repetitions of the vaporisation and condensation process, a mixture of concentration $x_n = y_{n-1}$ is obtained. As the composition of the mixture in the sump remains nearly constant during total reflux, the separation effect is increasingly intensified.

$$\alpha^n = \frac{y_n\,(1 - x_0)}{x_0\,(1 - y_0)} \quad (9)$$

y_n corresponds to the mole fraction of the more volatile component in the column head and x_0 to the mole fraction in the liquid in the distillation flask. These values can be determined from the refractive index. The relative volatility (separation ratio) α is 1.07 for a mixture of methyl cyclohexane and n-heptane. The number of theoretical trays can be calculated taking the logarithm

of (6). Graphically, the number of theoretical trays can be determined by plotting the curve in Fig. 4 for a relative volatility of 1.07 (broken line). Compared with a relative volatility of 2.0, a substantially larger number of separation steps is required to reach the same final concentration for the same initial concentration.