Chemical unit operations 2.

lectures 2 hours/week calculation seminars weekly 1 hours laboratory weekly 3 hours

Requirements

- Attendance will be checked.
- Requirements for the signature:
 - Attending on minimum 66% of the lectures and calculation seminars, and on all laboratory practices is required.
 - One calculation test will be scheduled during the semester. Exact dates and topics covered will be announced later. The calculation test have to be passed for signature. The grade of the calculation test counts as 25% of the final grade.
 - Nine laboratory measurements will be scheduled. Each measurement have to be performed, and reports accepted.
- Students having **valid signature** may take a **written exam** during the examination period. Application for the exams is only possible via the Neptun system.
- Website of the course: <u>http://kkft.bme.hu/oktatas/cuo2/</u> Please check it frequently!

Distillation

Edit Székely, Béla Simándi

Topics to be covered

- Distillation in the industry (introduction).
- Basic definitions. Vapour-liquid equilibria. Measurement and simply calculation methods. Ideal and non-ideal phase diagrams.
- Batch distillation.
- Flash distillation.
- Distillation columns = rectification.

Distillation in the industry

- Ethanol production
 - Food industry
 - Chemical industry
 - Bioethanol



Distillation in the industry

- Ethanol production
- Oil industry
 - fractionation

(products based on distillation intermediates: fuels, raw material of chemical industry, plastics, solvents, bitumen etc.)



Distillation in the industry

- Ethanol production
- Oil industry
- Waste water treatment
 - Mainly waste waters with high solvent contamination
 - Waters from absorption (purification of exhaust gases).



Advantages of distillation

- Major separation process for homogeneous liquids of two or more components.
- Separation is based on the difference in boiling points (volatility).
- No additional chemicals are needed, but energy requirement is relatively high.
- In a large number of separation task it is the most economical option.

Boiling point

- Depends on:
 - ingredients
 - molar ratios, exact composition
 - pressure

A liquid starts to boil if the sum of the partial pressure of its ingredients is equal to the pressure of the environment.

Vapour pressure of a pure component

- Vapour pressure is the pressure measured above a neat liquid component in equilibria (no other components in the system).
- It depends on the materials itself, and on temperature. Always increases with temperature.
- Antione equation:

$$\lg p^0 = A - \frac{B}{C+T}$$

- Po vapour pressure (Pa; Hgmm),
- T temperature (°C, K),
- A,B,C Antoine-constants

Volatility

- If its boiling point is lower at a chosen pressure than the other's one, that component is ^{*p*[bar]} called more volatile.
- If a liquid mixture is boiling, in general, the more voletile component has a higher relative concentration in the vapour phase than in the liquid phase.
- Volatility is the ratio of the molar fraction of component *j* in the vapour phase over its molar fraction in the liquid phase.

 $K_{j} = \frac{y_{j}}{\chi}$



Laws of Raoult and Dalton

Dalton's law

Partial pressure is the share of the given vapour of the total pressure. This is proportional with its molar fraction in the vapour phase. p_i partial pressure of component *j* (Pa), y_i molar fraction of component *j* in vapour phase (-), *P* total pressure (Pa).

$$p_j = y_j P$$

Raoult's law

A mixture is ideal from a practical point of view if law of Raoult is valid for any compositions in the examined range of temperatures. p_{i}^{0} vapour pressure of neat component j (Pa) at the given temperature, x_i molar fraction of component *j* in the liquid phase. $p_i = p_i^0 x_i$

Bubble point – dew point diagrams

• These diagrams are constructed based on experimental data obtained in special equipment.

Measurement of vapour- liquid equilibrium data



- The liquid is heated by electrical heating and kept continuous boiling. Pressure is stricktly kept constant.
- The vapour phase is circulated.
- At equilibrium samples are taken from both phases, and composition is analysed.

Bubble point – dew point diagrams

- These diagrams are constructed based on experimental data obtained in special equipment.
- In case of ideal mixtures, phase diagrams can be easily obtained by simple calculations.
- A mixture is ideal if:
 - Law of Raoult is valid,
 - Complete misciblity in liquid phase,
 - The constituents are usually chemically similar (e.g. linear chain hydrocarbons).



mixture of benzene and toluene at atmospheric pressure (*P*=1.013 bar)



mixture of isopropil-ether-isopropanol at atmospheric pressure



mixture of acetone-chloroform at atmospheric pressure



mixture of ethyl acetate – water at atmospheric pressure

Batch distillation



Batch distillation – mathematical description of the unit oparation Deriving the Rayleigh-equation

Set up the molar balance and component balance equations for an infinitely short d*t* time.

During this dt time, a vapour of molar amount dV is produced with a composition y (molar increase of distillate is equal, since distillate is formed by condensing the vapour). Molar amount of the boiling liquid in the vessel is meanwhile decreased by dL. Thus the molar balance is:

Rayleigh-equation

$$\mathrm{d}L = \mathrm{d}V = \mathrm{d}D$$

$$L \cdot x = (L - dL)(x - dx) + dV \cdot y$$
$$L \cdot x = L \cdot x - dL \cdot x - L \cdot dx + dL \cdot dx + dV \cdot y$$

neglect second-order differential dLdx and reorder:

$$0 = -dL \cdot x - L \cdot dx + dV \cdot y$$

substitute dL=dV

$$0 = -dL \cdot x - L \cdot dx + dL \cdot y$$

separate the variables

$$L \cdot dx = dL \cdot (y - x)$$
$$\frac{dx}{y - x} = \frac{dL}{L}$$
$$\int_{x_1}^{x_0} \frac{dx}{y - x} = \int_{L_1}^{L_0} \frac{dL}{L}$$
$$\frac{\int_{x_1}^{x_0} \frac{dx}{y - x}}{\int_{x_1}^{x_0} \frac{dx}{y - x}} = \ln \frac{L_0}{L_1}$$

Batch distillation – mathematical description of the unit operation Applications of the Rayleigh-equation

where

y and x are compositions of vapour and liquid phases in equilibrium; index 0 refers to initial (at t_0 time) 1 refers to the final (t_1) values; L is molar amount of the liquid phase (mol).

If initial amount of the liquid (L_0) and its composition (x_0) is known and the desired purity is defined (x_1) , amount of remaining liquid (L_1) can be calculated by the Rayleigh-equation.



Batch distillation – mathematical description of the unit operation Calculation of average composition in distillate

 L_0, L_1, x_0, x_1 are already known. From molar and composition balances the two unknown can be calculated.

$$L_0 = L_1 + D \Longrightarrow D = L_0 - L_1$$
$$L_0 \cdot x_0 = L_1 \cdot x_1 + D \cdot \overline{x}_D \Longrightarrow \overline{x}_D = \frac{L_0 \cdot x_0 - L_1 \cdot x_1}{D}$$

where \overline{x}_D is the average composition of distillate.

Applications of batch distillation

- Limits of separation. Subsequent distillations are needed.
- When relatively smaller amount of feed have to be purified batch distillation is more economic than continuous distillation processes.
- When composition of feed changes frequently, but distillation have to be performed in the same unit.

Continuous single stage distillation / flash distillation

- Consists of:
 - vaporizing a definite fraction of the liquid in such a way, that the evolved vapor is in equilibrium with the residual liquid,
 - separation the vapour and the liquid,
 - condensing the vapour.
- It is a continuous, steady-state operation.
 - steady-state: temperature, pressure, compositions and flow rates are constant.
- Separation performed is equivalent to one single theoretical stage.

Continuous single stage distillation at constant



Flash distillation by reduction of pressure



Flash distillation by partial condensation



Flash distillation – mathematical description

Molar balance F = L + V

Component balance $F \cdot x_F = L \cdot x + V \cdot y$

Express *y* as function of *x* and plot the expression in the equilibrium diagram!

Since *x* and *y* are equilibrium compositions, intersection of the two curves is the point of operation.

$$y = \frac{F \cdot x_F - L \cdot x}{V} = \frac{F}{V} x_F - \frac{F - V}{V} x = \frac{F}{V} x_F - \frac{L}{V} x$$

Flash distillation



Flash distillation – range of operation



Flash disitillation is one single equilibrium stage.

Flash distillation - summary

- Rarely used as individual separation unit because its limitations in purity.
- In case of non-ideal mixtures like heteroazeotropic mixtures it might be an option.
- Partial reboiler of a rectification column is a flash distillation unit.

Distillation columns – continuous rectification

- A separation process performed in steady state operation.
- As usual for continuous processes, it is mostly applied at constant and high feed rates.
- Frequently used in industrial scale.
- Separation is based on vapour-liquid equlibrium.

Rectification = subsequent partial condensations and subsequent partial evaporations

P=constant



Distillation column


Rectification, balance equations



Simple calculation methods for inital estimations

- The technique discussed is considered to be the simplest method for analysis of binary distillation.
- In an ideal stage (plate or tray), the V phase leaving the stage is in equilibrium with the L phase leaving the same stage.
- The problem is that of finding the number of ideal stages required in an actual column to achieve a desired separation.
- If the number of theoretical stages can be determined, and information on the stage efficiencies is available, the number of actual stages can be calculated.



Continuous fractionation column- Constant molal overflow

Assumptions:

- The column is adiabatic (sufficient insulation, neglectable heat loss).
- Heat effects (heats of solution, heat losses to and from column, etc.) are negligible.
- Heat of evaporation is the major source of any heat effects in the column.
- Molal heats of vaporization of the components are roughly the same. For every mole of vapour is condensed, a mole of liquid vaporized.

Results:

• Liquid and vapour molar flow rates are constant in the rectifying and in the stripping sections, separatly.



Continuous fractionationcolumn – reflux ratio, operating x_0 lines

Plates are numbered serially from the top down. Flows leaving the plates are numberred accordingly.

Assumption: liquid and molar flows leaving a theoretical (ideal) plate have equilibrium compositions.

Based on constant molal overflow:

$$V_1 = V_2 = \dots = V_n = V$$

$$L_0 = L_1 = L_2 = \dots = L_n = L$$



Rectifying operating line

Consider the part of the column enclosed by control line, a component balance of rectifying section can be written as:

 $V \cdot y_{n+1} = L \cdot x_n + D \cdot x_D$

Molar balance of the rectifying section (similar to the balance equation of the condenser): V = L + D

Expressing y_{n+1} from the component balance and substituting into molar balance equation we obtain:

$$y_{n+1} = \frac{L}{V} \cdot x_n + \frac{D}{V} \cdot x_D = \frac{L}{L+D} \cdot x_n + \frac{D}{D+L} \cdot x_D$$



Rectifying operating line

$$y_{n+1} = \frac{L}{V} \cdot x_n + \frac{D}{V} \cdot x_D = \frac{L}{L+D} \cdot x_n + \frac{D}{D+L} \cdot x_D$$
Divide by *D* and substitute the reflux ratio (*R*=*L*/*D*):

$$y_{n+1} = \frac{R}{R+1} \cdot x_n + \frac{x_D}{R+1}$$

Generalized form is an equation of a straight line:

$$y = \frac{R}{R+1} \cdot x + \frac{x_D}{R+1}$$



Operation line of the stripping section

Balance equations can be set analogously to the lower part of the column. Control line includes the still and all plates below plate *m*.

V' and L' are the molar flow rates of vapor and liquid in the stripping section:

L'=V'+W

$$L' \cdot x_m = V' \cdot y_{m+1} + W \cdot x_W$$



Operation line of the stripping section

L'=V'+W

$$L' \cdot x_m = V' \cdot y_{m+1} + W \cdot x_W$$

$$y_{m+1} = \frac{L'}{V'} \cdot x_m - \frac{W}{V'} \cdot x_W$$

$$y = \frac{L'}{V'} \cdot x - \frac{W}{V'} \cdot x_W$$



Continuous fractionation column – reflux ratio and operating lines

With known reflux ratio operating line of the rectifying section can be draw in the VLE (equlibrium) diagram.

The condition of the feed can be deduced by the slope of the feed line or q-line. The q-line is that drawn between the intersection of the operating lines, and where the feed composition lies on the diagonal line.

$$y = \frac{L'}{V'} \cdot x - \frac{W}{V'} \cdot x_W$$

Continuous fractionation column – feed line/ q-line

| $a = \frac{H_F - h_F}{H_F - h_F}$ | , where H_F is the enthalpy of the saturated |
|-----------------------------------|---|
| λ_F | vapour with the composition of x_F (J/mol), |
| | h_F is the enthalpy of the feed (J/mol), λ_F is |
| | molar heat of vaporization of a mixture with |
| | x_F composition (J/mol). |

| Consistence and properties of feed | h _F | q |
|--|---------------------------------|-----------|
| Cold liquid (below its boiling point) | $h_F < H_F - \lambda_F$ | 1 < q |
| known as subcooled liquid | | |
| Boiling liquid known as saturated liquid | $h_F = H_F - \lambda_F$ | q = 1 |
| Mixture of liquid and vapour, q is equal | $h_F = H_F - q \cdot \lambda_F$ | 0 < q < 1 |
| to liquid mole fraction | | |
| Saturated vapour | $h_F = H_F$ | q = 0 |
| Overheated (superheated) vapour | $h_F > H_F$ | q < 0 |



V

V'

11

 W, x_{W}

1

2

 F, x_F

 $V, \overline{y_{\rm f}} \xrightarrow{} \overline{} \mathcal{L}, \overline{x_n}$

When feed is miture of vapour and liquid, (q) liquid fraction is added to the liquid and (1-q) fraction to the vapour flow.

 $L' = L + q \cdot F$ $V = V' + (1 - q) \cdot F$

Continuous fractionation column – condition of feed

Deduct equation of rectifying operating line from equation of stripping operation line:

$$y = \frac{L'}{V'} \cdot x - \frac{W}{V'} \cdot x_W \Longrightarrow V' \cdot y = L \cdot x - W \cdot x_W$$
$$y = \frac{L}{V} \cdot x_n + \frac{D}{V} \cdot x_D \Longrightarrow V \cdot y = L \cdot x + D \cdot x_D \quad (-)$$
$$(V' - V)y = (L' - L)x - Wx_W - Dx_D$$
$$L' = L + q \cdot F \qquad ((q - 1) \cdot F)y = (q \cdot F)x - F \cdot x_F$$
$$V = V' + (1 - q)F \qquad (q - 1)y = (q)x - x_F$$
$$y = \frac{q}{q - 1} \cdot x - \frac{1}{q - 1} \cdot x_F$$

Knowing q the q-line can be drawn.



Minimal reflux ratio





Minimal number of theoretical plates

Simple calculation methods for inital estimations

- Calculation of the minimal number of theoretical plates.
 - gives us information about the difficultness of the desired separation,
 - needed: desired compositions of overhead and bottoms products.
- Minimal reflux ratio: to achive the desired separation, reflux ratio has a minimal value.
- Number of theoretical plates is determined: with McCabe Thiele method.





Simple calculation methods for inital estimations

- Calculation of the minimal number of theoretical plates.
 - gives us information about the difficultness of the desired separation,
 - needed: desired compositions of overhead and bottoms products.
- Minimal reflux ratio: to achive the desired separation, reflux ratio has a minimal value.
- Number of theoretical plates: with McCabe Thiele method.
- Calculation of column diameter.

$$F_{\text{load}} = v \sqrt{\rho_G}$$
$$\frac{\text{m}}{\text{s}} \cdot \sqrt{\frac{\text{kg}}{\text{m}^3}} = P a^{\frac{1}{2}}$$

$$\rho_G = \frac{P \cdot \overline{M}}{R \cdot T}$$

 $P = P_0 + \Delta P \cdot N_{\rm real}$

Load factor

- Load factor (F_{load}) :
- Depends on: linear velocity of vapour in the empty column (ν) density of vapour (ρ_G).
- Density of vapour is influenced by: average molar mass (composition!), temperature (P, x), pressure. Pressure is lowest at top, highest at bottom of column.

Plate efficiency



Operation range: horizontal part



Calculation of column diameter

$$v = \frac{F_{\text{load}}}{\sqrt{\rho_G}}$$

volumetric flow rate at top and bottom $\dot{V} = V \frac{\dot{R_{const}} \cdot T_t}{P_0} \dot{V} = V' \frac{R_{const} \cdot T_a}{P} \bullet$ $v = \frac{V}{A} = \frac{V}{\frac{D_o^2 \pi}{D_o^2 \pi}} = \frac{4\dot{V}}{D_o^2 \pi}$ between. $D_o = \sqrt{\frac{4\dot{V}}{...}}$

- Selection of load factor value,
- caluclate diameter at top and bottom (D_0) ,
 - select a suitable value in between.

 R_{const} is the ideal gas constant 8.314 J/(mol*K)

Simple calculation methods for inital estimations

- Calculation of the minimal number of theoretical plates.
 - gives us information about the difficultness of the desired separation,
 - needed: desired compositions of overhead and bottoms products.
- Minimal reflux ratio: to achive the desired separation, reflux ratio has a minimal value.
- Number of theoretical plates: with McCabe Thiele method.
- Calculation of column diameter.
- Calculation the height of the column.

Height of column

- Determine $(N_{\text{theoretical}})$.
- Read average plate efficiency (η_{plate}) and calculate the number of real plate. Round up.

$$N_{\rm real} = \frac{N_{\rm theoretical}}{\eta_{\rm plate}}$$

• Multiply with plate height.

$$H = N_{\rm real} \cdot \Delta H$$

Plate columns – topics covered

- Theoretical and real plates
- Operation
- Calculation of N_{\min} , R_{\min} McCabe Thiele method, plate efficiency
- Load factor
- Construction.

Bubble-cap plate







sieve plate



weir







Valve plate







Operation of valve trays





Packed columns

- Random or structured packing.
- Random packing is cheaper, but less efficient (same height less separation efficiency).
- Modern structured packing can be applied from laboratory scale to large industrial scales.

Determination of the heights of the column 1.

 $H = N \cdot \text{HETP}$

HETP= Height Equivalent to a Theoretical Plate



Sulzer Mellapak packing



Determination of the heights of the column 2.

- Instead of theoretical plates the term transfer units migh be also applied.
- NTU (Number of Transfer Units)
- HTU (Height of a Transfer Unit)
- To be calculated separatly for the upper and lower sections of the column. Only the active height is calculated.

$$H = \mathrm{HTU}_{1} \cdot \mathrm{NTU}_{1} + \mathrm{HTU}_{u} \cdot \mathrm{NTU}_{u}$$



Vmolar flow rate of vapour at top of column (mol/s), K_y mass tranfer coefficient (mol/(m²·s)),arelative surface area of packing (m²/m³), Φ wetting coefficient(-),Across section of column (m²), $y^* = mx$ virtual vapour concentration which would be in
equilibrium with the liquid concentration (-).
Theoretical background – the two film theory



Calculation of the heights of the column vapour condenser fiquid D, x_{D} $V \cdot dy = K_y \cdot a \cdot \Phi \cdot A \cdot (y^* - y) \cdot dH$ packing $dH = \frac{V}{K_v \cdot a \cdot \Phi \cdot A} \cdot \frac{dy}{y^* - y}$ *y* x F, x_{F} $H = \int_{\Omega}^{H_f} \mathrm{d} H = \frac{V}{K_v \cdot a \cdot \Phi \cdot A} \int_{v_r}^{v_r} \frac{\mathrm{d} y}{y^* - y}$ packing $HTU_{u} = \frac{V}{K_{v} \cdot a \cdot \Phi \cdot A} \qquad NTU_{u} = \int \frac{dy}{y^{*} - y}$ vapour $\underbrace{HTU_l}_{\text{reboiler}} = \frac{V'}{K_y \cdot a \cdot \Phi \cdot A} \qquad NTU_l = \int_{v_w}^{y_F} \frac{\mathrm{d} y}{y^* - y}$ liquid reboiler

Calculation of HTU

known: F, R, q, x_F , x_D , x_W F = W + D $F \cdot x_F = W \cdot x_w + D \cdot x_D$ $F \cdot x_F = W \cdot x_w + D \cdot x_D = W \cdot x_w + (F - W) \cdot x_D$ $W = \frac{F(x_F - x_D)}{x_W - x_D}$ D = F - W $V' = V + (q-1) \cdot F$ $V = (R+1) \cdot D$ $HTU_{l} = \frac{V'}{K_{v} \cdot a \cdot \Phi \cdot A}$ $HTU_{u} = \frac{V}{K_{v} \cdot a \cdot \Phi \cdot A}$

Calculation of NTU



Random packing



Random packing / rings













Cascade ring

Raschig-ring

Pall-ring

Random packing / saddles







Super intalox-saddle

Berl-saddle



Further random packing elements









Snowflakes



Konjugated rings

Lessing-ring

Further random packing elements





Envipack spheres



balls



Spiral packing



| Sulzer packing | 1 |
|--------------------------------|----|
| in various types and different | |
| materials | |
| | |
| Support grid | 2 |
| for the packing | |
| | |
| Liquid collector | 3 |
| | |
| Feed nine | 4 |
| te distributor | - |
| to distributor | |
| | - |
| Liquid distributor | 5 |
| mounted on locating grid | |
| | |
| Locating grid | 6 |
| | |
| Steam inlet pipe | 7 |
| | |
| Column sump | 8 |
| | |
| Circulation nine | 9 |
| to rehailer | |
| to reponer | |
| | |
| Skirt | 10 |
| | |
| Anchorage | 11 |
| | |
| | |
| Variations on the above design | |
| Feed: | |
| | |

- vapor
- two phases with flash box
 Side stream:
- · liquid from collector
- · vapor collector



Structured packing





Structured packing types of distillation











Liquid distributors



Grids





Locating grids





photos: Sulzer



Economical optimum

$$\dot{Q}_{\text{reb}} = V'\lambda_W =$$

$$= \left[V + (q-1)F\right]\lambda_W =$$

$$= \left[(R+1)D + (q-1)F\right]\lambda_W$$

 $\dot{Q}_{\text{cond}} = V\lambda_D =$ = $(R+1)D\lambda_D$



Thank you for your attention!