

Practica in Process Engineering II

Extraction

Introduction

Extraction is a process in which one or more components are separated selectively from a liquid or solid mixture, the feed (Phase 1), by means of a liquid immiscible solvent (Phase 2). The transfer of the components from the feed to the solvent is controlled by the solubility behavior of each component in the corresponding phase. Two phases result from the extraction step: one enriched (EXTRACT Phase) and the other depleted (RAFFINATE Phase) in the components to be separated, respectively. Afterwards in order to regenerate the solvent, another separation step (e.g. distillation) is finally required. Liquid-liquid extraction is most widely used and will be considered within this laboratory. It is applied e.g. to remove heavy metals or acids from waste water or for the production of aromatic compounds from mixtures of hydrocarbons. Another application is gas-liquid extraction which is also called absorption.

Figure 1 shows the four streams involved in the extraction process with the common nomenclature in the case when component B is separated from the mixture of A and B by means of a solvent C, i.e. $AB + C \rightarrow A + CB$. This nomenclature will be kept during the whole theoretical part of this handout.

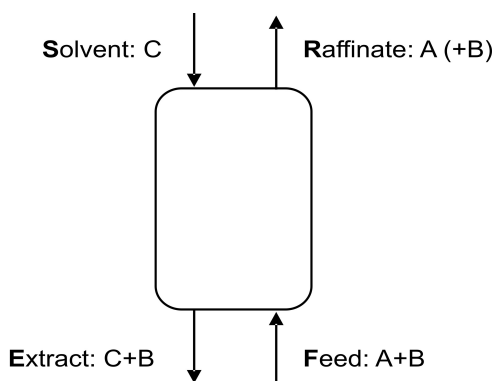


Figure 1: A typical extraction step.

Compared to distillation, extraction processes have the disadvantage that a new component is added to the system. This leads to additional impurities as complete immiscibility does only exist in theory. Furthermore a subsequent separation process is required to regenerate the solvent. However, there are a number of situations in which extraction is advantageous and they are summarized in the following:

- One or more components in the mixture are not thermally stable.
- The components in the mixture have a very high or low boiling point requiring vacuum or cryogenic distillation, which is very energy intensive.
- The boiling points of the components are very close or they form azeotropes.

- Two components with very different boiling points have to be separated at the same time.
- The components to be separated (pollutants or valuable products) are only a small fraction of the mixture.

If you have not attended any course about extraction yet, it is highly recommended to have a look at the Hyper-TVT homepage [1], which explains briefly the concept of counter flow extraction columns (Section “Liquid-liquid extraction”)!

Theoretical background

The concept of extraction: the one stage extractor

The simplest form of an extractor apparatus has only one stage and the process is performed in two steps. In the first step, the feed is mixed with the solvent to create a high surface area allowing to achieve high mass transfer rates. The mass transfer stops when thermodynamic equilibrium between the two phases is reached. Equilibrium is characterized by an equal temperature, equal pressure and equal chemical potentials in both phases. In the second step the two phases are allowed to separate (settling process). Finally, after decanting one receives the raffinate and the extract. Figure 2 illustrates the concept.

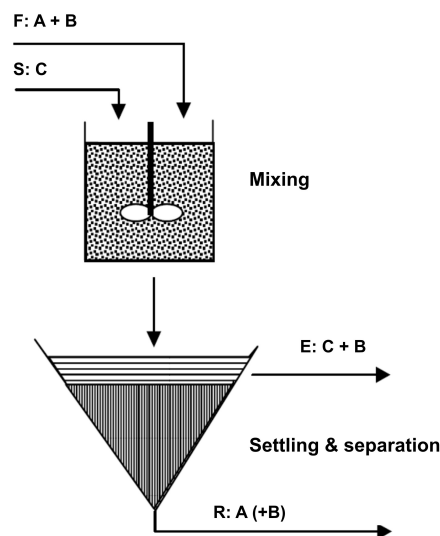


Figure 2: The one-stage extractor.

To allow an optimal extraction process, it is crucial to ensure a good mixing between the solvent and the feed, to have enough contact time between the two phases and to give enough settling time to separate the two phases. Considering this process, a number of requirements for a suitable solvent C can be specified:

- high capacity for component B
- high selectivity for component B
- low solubility in A (and vice versa)

- simple separation between B and C
- considerable difference in the densities compared to A
- low surface tension
- low viscosity
- chemical and thermal stability
- nontoxic
- no or low corrosivity
- low cost

However, in order to obtain the required separation several steps of mixing and phase separation are mostly needed. Therefore, in practical applications multi-stage extractors are usually used. As for many separation processes, a co-, a cross-, or a counter-flow concept can be applied [1]. Some of the important aspects for designing multi-stage extractors are discussed in the following sections.

Multistage exercise and 3-component diagrams

In this exercise, we will discuss how to combine thermodynamic data (represented by a 3-component-diagram) with a mass balance in order to design an extraction process. In our case, we have an aqueous phase (water), an organic phase (toluene) and a component (acetone) which is meant to be extracted. Please note that for educational purpose, the acetone concentration in this exercise is much higher than during your experiments (safety concerns).

3-component-diagrams

Have a look at the diagram (handed out during the experiments):

- Where are the pure components?
- Where is only one phase, where are two phases?
- What is the name of the lines crossing the diagram?
- Where can one find the following compositions (all values as % mol):
A: 15% H_2O , 10%*Toluene*, 75%*Acetone*
A: 40% H_2O , 50%*Toluene*, 10%*Acetone*

1-stage extractor

As production engineer, you are responsible for a pharmaceutical plant, where toluene is used as a solvent. Acetone is added to receive a final mixture of 5% mol acetone. Unfortunately, one of your employees poured too much acetone into toluene because he was distracted by a young accountant passing by, so that you find a mixture of 30% mol acetone and 70% mol toluene (50 kg in total). The unwanted acetone has to be removed. You decide to use water as an extraction agent. Your employee can add the water, mix it well and decant the two phases afterwards. How much water does he have to add?

cross current extractor

After yesterday's accident you are fascinated by extraction and order your employee to prepare the same mixture as yesterday. However, this time you will use a 3-stage cross flow extractor. For every stage you will add approximately one third of the water that you added in the previous one stage process. You are really curious to find out if you can reach an even lower acetone concentration?

- Draw a short scheme of the cross flow process
- Solve the problem graphically (use diagram)

counter current extractor

As your CEO finds your results very interesting too, he orders you to design an extractor for a continuous flow of $100 \frac{kg}{h}$ of the 30% mol acetone and 70% mol toluene mixture. The final acetone concentration must not exceed 5% mol. The feed to water ratio shall be 1:4 in moles.

- How many stages will be needed?
- After a graphical solution, check your streams and compositions by using a mass balance!

General questions on extraction

- What is the main problem of extraction?
- In which cases is it a good idea to use extraction?
- Draw two 3-component-diagrams: One for a system where extraction is not possible, one diagram where extraction should work!
- Discuss the effect of the slope of tie lines on extraction!

Hydrodynamics

A high specific surface allows to increase the mass transfer, thus improving the extraction efficiency. The common method is to generate small droplets of one phase that are dispersed in the other, continuous phase, as in the stirred column used in this laboratory. Interactions between droplets and droplets and with the continuous phase result in complex fluid dynamic problems that are usually treated using empiric equations. Main factors to be considered for the operation of an extraction column are:

- **Droplet size:** Droplets usually range into the mm region. Big droplets can not provide a sufficient sized specific surface, whereas smaller ones result in high demand of energy for the dispersion process. Furthermore, the velocity of the droplets decreases with decreasing size; the operating limit of the column is reached when the droplets are too small to move and it is defined as the flooding point.
- **Droplet size distribution:** A uniform droplet size distribution is desired in order to increase efficiency. Furthermore due to the fact that most calculations are done with a mean droplet diameter the results are more accurate for a uniform droplet size distribution. However, the droplet size may change along the length of the column.

- **Holdup:** The total volume of all droplets (or the volume of the disperse phase) divided by the total column volume is called holdup ϵ . If operation conditions are set close to the flooding point of the column, the holdup increases and may not be stabilized any more.

$$\epsilon = \frac{V_{disperse}}{V_{disperse} + V_{continuous}}$$

- **Axial dispersion:** Axial dispersion follows from different phenomena, e.g. turbulence or differences in the droplet sizes, and results in lower column efficiency.

All these factors prevent a direct modeling approach of an extraction process, which is therefore usually designed with the help of empiric models. Two common design techniques will be discussed briefly.

Design concepts for multi stage extractors

As for the most thermal separation processes, two design techniques can be distinguished:

- based on mass transfer.
- based on equilibrium stages.

The design based on mass transfer is mathematically more complex and requires more information about hydrodynamics and property data. The calculation in a simplified case is discussed below. For the design based on equilibrium stages several methods exist, which differ in their assumptions and therefore in the accuracy and modeling complexity. The main methods are:

- McCabe-Thiele diagram (graphical).
- Kremser equation (analytical).
- graphical method in the ternary diagram.
- rigorous process simulation (e.g. Aspen).

Below only the method applying the McCabe-Thiele diagram is discussed. During the laboratory a short introduction to the method using the ternary diagram will be given and can be found in [1]. For the McCabe-Thiele method as well as for the simplified mass transfer calculation it is assumed that the phase flows are constant over the whole column. Therefore mass loadings ($Y : [\frac{\text{kgB}}{\text{kgA}}]$, $X : [\frac{\text{kgB}}{\text{kgC}}]$) and mass flows of A (called \dot{F}) and C (called \dot{S}) are used in the following. Assuming very low solubility of A and C, the flows \dot{F} and \dot{S} can be assumed constant.

HTU-NTU concept - a mass transfer concept

If the volume of a column can be regarded as a continuum, average mass transfer exchange rates are used for design purposes. In the easiest case, one assumes that two non-miscible flows are passing each other as plug flows along the column. Phase velocities are regarded as constant over the whole length of the column. Using a differential balancing approach and integration over the whole length of the column yields in:

$$H = \frac{\dot{S}}{K_X a A} \int_{X_{out}}^{X_{in}} \frac{1}{X - X^*} dX = \frac{\dot{F}}{K_Y a A} \int_{Y_{in}}^{Y_{out}} \frac{1}{Y^* - Y} dY$$

where H is the height of the column, A the cross section of a column, a the specific surface, K_X and K_Y the mass exchange coefficients, and X^* and Y^* are phase equilibrium loadings (X^* is the loading of the solvent phase in equilibrium with the actual loading of the feed phase and vice versa).

Referring to the solvent phase, the term $\frac{\dot{S}}{K_X a A}$ is called HTU which stands for height of a transfer unit. The integral is called NTU which stands for number of transfer units. The same is true referring to the other phase, which results in different numbers for the NTU and HTU values. The NTU integral is usually solved numerically. It describes the thermodynamic separation behavior and is a measure how difficult the separation is. Typically, Y^* is expressed as a function of X . The HTU value depends on the flows and the column parameters (specific mass transfer area etc.) and describes how effective the column works. Knowing both values the required height of a column can be calculated $H = \text{HTU} \cdot \text{NTU}$.

Equilibrium stage concept

Comparable to distillation or absorption, the McCabe-Thiele diagram can be used in extraction to determine graphically the theoretical number of equilibrium stages. This requires the knowledge of the equilibrium line and the operating line. The equilibrium loading Y^* is generally given as a function of X :

$$Y^* = f(X)$$

By means of a mass balance of component B the operating line can be calculated:

$$Y = Y_{in} + \frac{\dot{S}}{\dot{F}}(X - X_{out})$$

Figure 3 illustrates a typical construction in a McCabe-Thiele diagram. It is worth repeating that loadings ($Y : [\frac{\text{kg}_B}{\text{kg}_A}]$, $X : [\frac{\text{kg}_B}{\text{kg}_C}]$) instead of mole fractions are used and that for the operating line the pure mass flows of A (called \dot{F}) and C (called \dot{S}) are taken.

Once the number of theoretical equilibrium stages N_{eq} is known, the HETS value (HETS: height equivalent of a theoretical stage) or the efficiency of a real stage η can be used to calculate the column height H or the number of real stages required N , respectively:

$$H = \text{HETS} \cdot N_{eq}$$

$$N = \frac{N_{eq}}{\eta}$$

Please note that in our case, we are **NOT** using an **equilibrium stage** column as we do not have separated stages. In our case, the column is comparable to a constant counter-current stream with zones of higher and lower mixing intensity.

Experimental part

In the scope of this lab course, the toluene-acetone-water system will be considered, i.e. acetone (B) will be extracted from toluene (A) with the solvent water (C). The equilibrium of this system

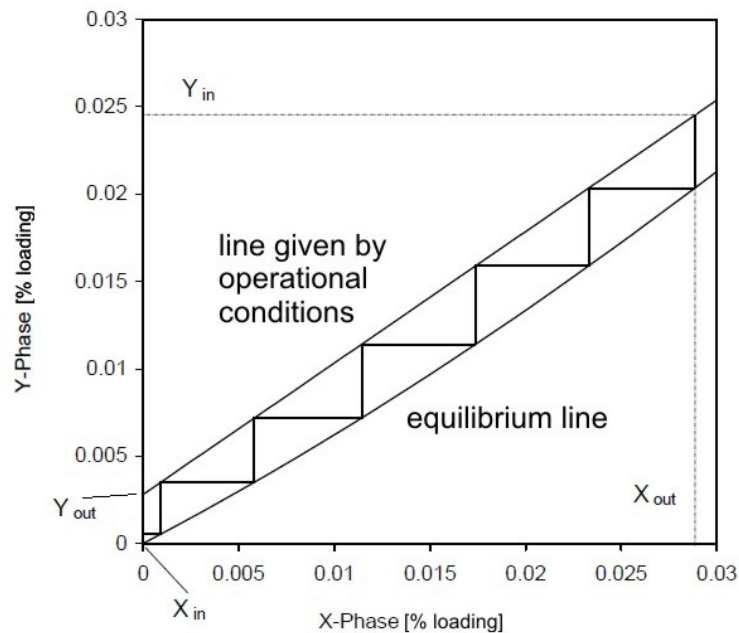


Figure 3: McCabe-Thiele diagram with equilibrium and operating line.

is given by the following equation:

$$Y^* = 0.573X + 5.066X^2 - 17.17X^3$$

The experimental setup and procedure will be described in the following sections.

Laboratory equipment

Figure 4 shows a scheme of the laboratory setup.

A stirred column (1) is used for the extraction (column type Oldshue-Rushton). Two tanks (3) hold the feed (toluene and acetone) that is pumped (5) to the column, fresh water from the tap is used as the solvent. Several valves and pumps (5) allow for setting up different experiments. Flow rates are indicated by rotameters (4). The filling level of the column is being controlled by a siphon (7). Once the toluene has left the column it flows through a (safety) water separator (6) and back to the tanks (3). As toluene has a lower density, the toluene flow direction is from bottom to top. For safety reasons, the continuous phase is always water and the organic phase toluene is dispersed. More details about the operation will be given during the laboratory. During start-up and shut-down of the equipment as well as when you reach the flooding point (stirring speed > 250 rpm) an assistant should be always at the column!

Measurements

During the laboratory, two issues will be investigated. The first part deals only with hydrodynamics whereas in the second one the extraction performance is studied. For both parts the flow rates are kept constant at $30 \frac{l}{h}$ and $20 \frac{l}{h}$ for toluene and water respectively.

1. The **holdup** will be measured at different stirring speeds. For this the glass valve in the lower half of the column is opened and a 100 ml cylinder is filled with dispersion.

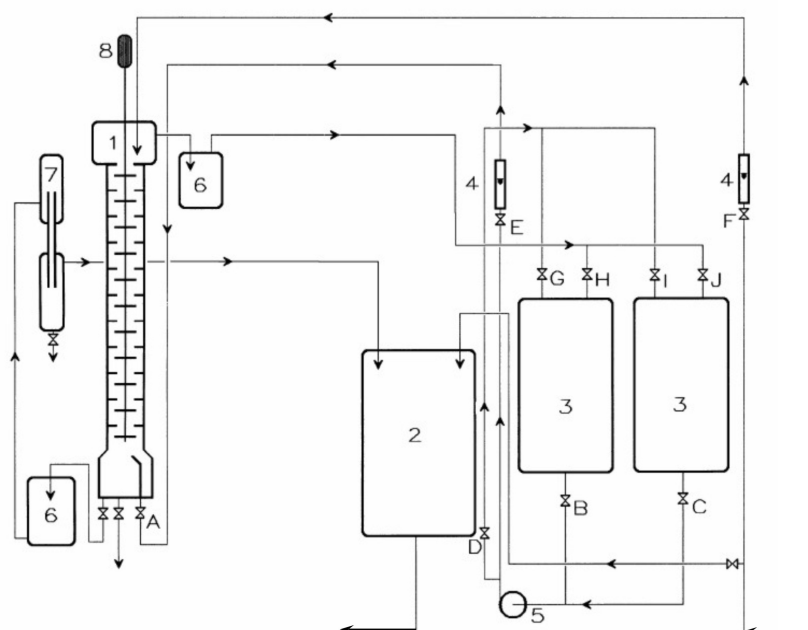


Figure 4: 1: column, 2: tank (aqueous), 3: tank (organic), 4: rotameter, 5: pump, 6: decanter, 7: filling level control, 8: stirrer motor.

After waiting for settling of the two phases, the volume of toluene and the total volume is measured. This measurement is repeated at stirring speeds of 50, 100, 150, 200, and 250 rpm. After changing the stirring speed the conditions in the column have to reach a steady state, therefore it is important to wait for about 15 minutes before taking the next sample. At stirring speeds slightly larger than 250 rpm the column is expected to reach flooding conditions. Therefore, after taking the sample at 250 rpm the stirring speed is increased very slowly until the flooding point is reached (an assistant should be at the column). For this part only water and toluene (without acetone) are used.

2. The **extraction performance** is studied at different stirring speeds. Acetone is added to the toluene to obtain a concentration of approx. 2-3 wt%. The stirring speed is increased stepwise (50, 100, 150, 200, and 250 rpm) and samples from the two outlet streams are taken. Additionally, one sample is taken from the feed in order to obtain its exact composition. The samples can be taken from the pipes using a syringe at the provided places. The samples are collected in vials and will be analyzed by GC during the following week. Please note that due to the high volatility of acetone, samples have to be sealed.

Report

After the successful completion of the laboratory work, a short report has to be prepared. The report should consist of the following sections:

- Introduction and brief explanation of extraction as a separation process (about 1 DIN A4 page).

- Experimental procedures and setup (about 1 DIN A4 page).
- Results and discussion (detailed analysis of the experiments). This section should give a comprehensive answer to the following questions:
 1. Plot the hold-up versus the stirring speed.
 2. Do you expect an increase or a decrease of the hold-up with increasing stirring speed? Based on the theoretical part during the laboratory course, explain why you expect a decrease or an increase.
 3. Is the plot in line with your expectations? If not, specify the measurements that don't match with the expectations. What could be the causes for the deviations?
 4. Do you always expect a better purification of your feed stream by increasing the stirring speed?
 5. Plot the extract and raffinate composition versus the stirring speed. Does the plot confirm your expectations?
 6. For the 5 operating points, determine the number of theoretical stages (NTS) with the McCabe-Thiele method.
 7. Calculate the slopes of the operating lines for the 5 operating points. Which value do you expect? What could be reasons for possible deviations?
 8. Plot the number of theoretical stages versus the stirring speed.
- Perform a theoretical analysis of an extraction process by solving the exercise presented earlier on page 3 and 4.

Data

Densities

- Density of water: $998 \frac{kg}{m^3}$
- Density of toluene: $866 \frac{kg}{m^3}$
- Density of acetone: $790 \frac{kg}{m^3}$

The extraction column

- Length of the stirred section: 1 m
- Column diameter: 73 mm; Stage height: 50 mm
- Free cross section area of the stators: 38 %
- Number of stirrers: 19
- Stirrer diameter: 50 mm; Stirrer height: 10 mm

Rotameters

The two rotameters have been calibrated for water and toluene. Figure 5 can be used to determine the set-value of the rotameters at the desired volume flows.

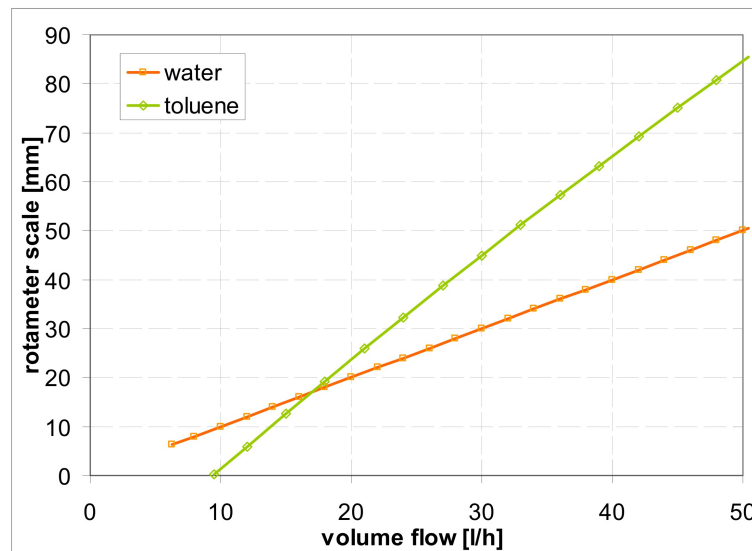


Figure 5: Rotameter calibration data.

References

- [1] Mazzotti, M.: "*Hyper-TVT*": <http://www.hyper-tvt.ethz.ch/extraction-page.php>", ETH, Zuerich, 2009.
- [2] Wankat, P. C.: "*Separation Process Engineering*", Chapman and Hall, London, 2006.

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