Simulation and Design of Packed Extraction Column

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SYMBOLS

\(a\) total surface restricting the movement of a drop, \(m^2 \cdot m^{-3}\)
\(a_i\) interfacial area, \(m^2 \cdot m^{-3}\)
\(a_p\) total packing surface per volume of column, \(m^2 \cdot m^{-3}\)
\(a_s\) interfacial area due to static holdup, \(m^2 \cdot m^{-3}\)
\(A_c\) cross section area of the column, \(m^2\)
\(A_{pr}\) projected area of sphere, \(m^2\)
\(c\) concentration of solute, \(kg \cdot m^{-3}\)
\(c^*\) concentration of solute in equilibrium, \(kg \cdot m^{-3}\)
\(C_D\) drag coefficient, -
\(d_{sv}\) Sauter mean drop diameter, \(m\)
\(d_{fr}\) ratio of dispersed and continuous phase flooding velocities, -
\(D_c\) molecular diffusion coefficient, \(m^2 \cdot s^{-1}\)
\(D_{ax}\) axial dispersion coefficient, \(m^2 \cdot s^{-1}\)
\(h\) length of the cone during drop formation, \(m\)
\(H\) total length of the drop formation, \(m\)
\(HTU_{ac}\) height of the transfer unit based on the continuous phase, \(m\)
\(K_{ac}\) overall mass transfer coefficient based on the continuous phase, \(m \cdot s^{-1}\)
\(K_{aw}\) overall mass transfer coefficient based on the water phase, \(m \cdot s^{-1}\)
\(k_c\) individual mass transfer coefficient based on the continuous phase, \(m \cdot s^{-1}\)
\(k_d\) individual mass transfer coefficient based on the dispersed phase, \(m \cdot s^{-1}\)
\(L\) length of the packing surface, \(m\)
\(m_{dc}\) distribution coefficient based on a concentration driving force, -
\(m_{dc}^*\) distribution coefficient based on a concentration driving force, -
\(\dot{n}\) molar flow of the transitional component, \(mol \cdot s^{-1}\)
\(N_c\) mole flux of the transitional component in the continuous phase, \(mol \cdot m^{-2} \cdot s\)
\(N_d\) mole flux of the transitional component in the dispersed phase, \(mol \cdot m^{-2} \cdot s\)
\(N_{dr}\) number of drops in the contacting section, -
\(NTU_{ac}\) number of the transfer units based on the continuous phase, -
\(Q_c\) flow rate of the continuous phase, \(m^3 \cdot s^{-1}\)
\(Q_d\) flow rate of the dispersed phase, \(m^3 \cdot s^{-1}\)
\(r_1\) principal radius of curvature, \(m\)
\(r_2\) principal radius of curvature, \(m\)
\(R\) dispersion rate, \(mol \cdot s^{-1}\)
\(Re_c\) Reynolds number based on the continuous phase, -
\(S\) distance of the drop path, \(m\)
\(Sc_c\) Schmidt number based on the continuous phase, -
\(Sc_d\) Schmidt number based on the dispersed phase, -
\(Sh_d\) Sherwood number based on the dispersed phase, -
\(t_{dr}\) residence time of the drop, \(s\)
$U_{cf}$ flooding velocity of the continuous phase, m s$^{-1}$
$U_{df}$ flooding velocity of the dispersed phase, m s$^{-1}$
$U_{ic}$ interstitial velocity of the continuous phase, m s$^{-1}$
$U_s$ slip velocity, m s$^{-1}$
$U_{so}$ slip velocity at low dispersed phase flow rate, m s$^{-1}$
$U_t$ velocity of the drop, m s$^{-1}$
$V_d$ volume of the drop, m$^3$
$V_1$ volume of hemisphere, m$^3$
$V_2$ volume of cone, m$^3$
$z$ height of the column, m
$Z$ vertical path of the drop, m

**Greek symbols**

$\Delta \rho$ density difference, m$^3$ kg$^{-1}$
$\varepsilon$ void fraction of packing, -
$\chi$ tortuosity factor, -
$\eta$ drop size correction factor, -
$\theta_a$ angle of ascent of droplet, -
$\mu$ liquid viscosity, kg m$^{-1}$ s$^{-1}$
$\rho$ liquid density, kg m$^{-3}$
$\eta$ interfacial tension, N m$^{-1}$
$\phi_d$ dispersed phase holdup, -
$\phi_s$ static holdup, -
$\Phi$ parameter defined by Eq. (51), -

**Subscripts**

c continuous phase
d dispersed phase
E entrance section of the column
L the last discrete section of the column
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1 INTRODUCTION

Liquid-liquid extraction is a separation method, which is used to recover desired or to remove unwanted components from a crude liquid solution. It is a frequently used technology, which is utilized in the processing of a wide range chemicals, such as petrochemicals, metals, pharmaceuticals and wood derived chemicals. Liquid-liquid extraction is also widely used in other industrial processes, such as wastewater treatment and in food processing. [1]

The main principles of liquid-liquid extraction are introduced briefly in this work. Moreover, a short review of common extraction equipment, such as mixer-settlers, sieve-plate, spray and packed columns is given. The packed columns are studied in more detail by simulation at the end of this work.

The aim of this work was to simulate and design a counter-current packed liquid-liquid extraction column, which separates an acid from aqueous liquid to an organic solvent. The simulation and the design were done by a computer code with MATLAB and the results are introduced in the applied part of this work. The modeling of the column is based on Seibert’s and Fair’s research [2], Hydrodynamics and Mass Transfer in Spray and Packed Liquid-Liquid Extraction Columns, in which Seibert and Fair investigated mass-transfer efficiencies and hydraulic characteristics of a 10.2-cm packed column. In addition, mechanistic models, which represent the experimental findings of hydrodynamic and mass-transfer, are developed by Seibert and Fair. These models are also presented in this work.

2 LIQUID-LIQUID EXTRACTION

Liquid-liquid extraction is a separation method, which is used to recover a valuable or to remove an unwanted product from a solution which consists of two or more components (a multicomponent solution). The separation is performed by an immiscible solvent that is in contact with the solution. The product is separated from the solution to solvent that has a high affinity for the product. The solvent can be also a mixture of solvents instead of a single solvent. The phase from
which the product is taken off (the phase of the solution) is called raffinate and the phase which receives the product (the phase of the solvent) is called extract. [3]

Liquid-liquid extraction is an alternative to distillation processes when a liquid-liquid separation method is needed. Liquid-liquid extraction is often used when a product has to be removed from water. If the boiling point of this product is higher than water, all the water has to be distilled away which is often economically not feasible. However, if the boiling point is lower than water distillation can be used. In recovery by extraction process, the valuable product has to be also separated from the solvent and the solvent must be recovered for reuse (by distillation or some other method). This extraction-distillation combination is often more expensive than only distillation without extraction. Anyway, liquid-liquid extraction has a greater flexibility in choice of operational conditions than distillation. For example, the amount and the type of the solvent can be varied as well as the operating temperature. [3]

In addition, liquid-liquid extraction is used when separation by distillation would be difficult or ineffective. This kind of situation occurs when the liquids have boiling points near to each other. For example, one of the major uses of liquid-liquid extraction is to separate the products of the oil refining which have different chemical qualities but almost the same boiling range. [3]

3 EXTRACTION EQUIPMENT

In liquid-liquid extraction an equipment is needed which brings two phases into good contact with each other in order that mass transfer is efficient between the phases. In some extraction equipment the contact of the phases is improved by mechanical mixing because the energy required for mixing of two phases, which have comparable densities, is small. [3]

Liquid-liquid extraction equipment can be operated either continuously or batch-wise. In batch-wise equipment a quantity of feed liquid is mixed with a quantity of solvent, for example in an agitated vessel. After mixing and settling the layers of phases are separated. The extract is the phase of solvent plus the product and the raffinate is the phase of solution, from which the product has been removed.
The previous operation can be repeated if more than one contact time is needed. Usually, when several contact stages are required, continuous flow becomes more attractive and economical. [3]

Extraction equipment can be classified to mixer-settlers or vertical extraction towers, in which the separation is based on continuous flow or mechanical mixing. The principles of mixer-settlers and some vertical extraction towers are introduced next. [3]

3.1 Mixer-settlers

Mixer-settlers are liquid-liquid extraction equipment which can be operated batch-wise or continuously. In batch-wise extraction the mixer and the settler may operate in the same unit. Usually a tank, which contains a turbine or propeller agitator, is used. When the mixing stage is completed, the mixer is stopped and the phases are allowed to settle and separate by gravity. After that, the extract and the raffinate are removed to their own vessels. The times needed for mixing and settling are determined experimentally. [3]

Usually several contact units are needed so that sufficient separation is achieved. In that case, a train of mixer-settlers, which are operated with counter-currently, is used as shown in Figure 1. The raffinate from each settler is the feed to the next mixer in which it is separated from extract which is partly or total pure. [3]

In a continuously operated mixer-settler the mixer and the settler are separated to their own units. The mixer is usually an agitated tank which has inlets, outlets and baffles, but it could be also a static mixer. The settler is often a simple gravity decanter. [3]
3.2 Spray and packed columns

In spray and packed columns separation is operated continuously and simultaneously without stage contacts. The lighter liquid is fed at the bottom of the column and distributed as small drops. The drops rise and flow through the heavier liquid, which flows down as a continuous stream. The heavier stream leaves at the bottom of the column and the drops at the top of the column. The heavier liquid can also be the dispersed phase. In this case, the direction of the flows is reversed. The heavier liquid is dispersed into the light phase at the top of the column and the drops flow down through the lighter liquid, which is now a continuous stream. [4]

Mass transfer between phases is continuous and the composition of phases changes through the column. There is no equilibrium between phases because it is the difference from equilibrium which is the driving force for mass transfer. Mass transfer is the most efficient when the phases are in good contact with each other and this happens in the region, in which the drops are formed. That is why the drops are usually reformed at frequent intervals throughout the column. In Figure 2 a packed column is presented in which the reforming of the drops can be done by packing and a redistributor which are placed inside of the column. The packings such as rings, saddles or structured packings coalesces and reforms the drops and limits axial dispersion. [3,4]
The choice of the dispersed phase depends on the characteristics of the liquids and the operational parameters, such as the flow rates, for example [4]. Some important factors that the dispersed phase should have are: The dispersed phase should have a higher viscosity than the continuous phase, since a low viscosity of continuous phase makes possible a higher phase throughput. The dispersed phase should also have higher flow rate to obtain a maximum mass transfer area. A low interfacial tension between liquid and vapor is also an important factor for the dispersed phase. The low interfacial tension makes the dispersion possible easily. In any case, the choice of the dispersed phase cannot only base on theoretical considerations. Theories are good aid to experiments which are made, for example, in a pilot column with a real material system. [5]

3.3 Sieve-plate columns

In sieve-plate extraction columns the reforming of the drops is done by perforated plates like in sieve-plate distillation columns. In this way the axial mixing of an open column can also be limited. The diameter of the perforations in an extraction column are usually 1.5 - 4.5 mm and plate spacing range varies from 150 to 600
mm. The light liquid is usually the dispersed phase and the heavier liquid, continuous phase, flows through downcomers from upper plate to the next. The light liquid forms a thin layer under each plate and the layer is dispersed into the layer of heavy liquid above by perforations. This is shown in a Figure 3. [3,4]

Figure 3. A sieve-plate extraction column with downcomers and perforated plates [3].

4 MODELING OF PACKED EXTRACTION COLUMNS

Modeling of packed extraction columns can be divided into three main groups. One of these is empirical modeling which is based on experiments, which predict mean drop size and dependence of column geometry from operational conditions, for example. These models are simple and efficient but the models can be applied often only to some applications. Extraction columns can be also modeled by stage-wise modeling. Then an extraction column is described by a series of mixed stages. These stages can be, for example, cascades which model a differentially varying system, like a packed extraction column. The third alternative method to the modeling is differential modeling. It consists of differential conservation equations for liquid phases and it is subdivided to pseudo-homogenous and population balance models. [6]

Dynamic differential modeling with Seibert’s and Fair’s experimental models for drop size and phase holdups is used in the applied part of this work. The dynamic model is a differential dispersion model, which reflects the physical behavior and mass transfer of counter-current packed spray column [5]. The complex mathematical model is solved numerically by a computer code with MATLAB.
4.1 Hydrodynamics and Mass Transfer

To obtain a large mass-transfer area between two liquid phases (raffinate and extract), another phase has to be dispersed into drops. Seibert and Fair have determined models and coefficients for mass transfer, drop hydraulics and phase holdup, which are represented next.

4.11 Drop diameter

In the real column uniform drops are not formed, which is difficult to model mathematically. With a suitable model, behavior of the drops can be approximated. [5]

Seibert and Fair assume that the drops of the dispersed phase are spherical and the drop size can be determined by a model, which contains two principal radii of curvature \( r_1 \) and \( r_2 \) as illustrated in Figure 4. The pressure difference across the interface of the phases is given by Young-Laplace equation

\[
\Delta P = \sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right)
\]

(1)

where \( \sigma \) is the interfacial tension of the phases.

It is supposed, that the curvature \( \frac{1}{r_2} \) is relatively small and can be neglected. Besides, the radius of curvature \( r_1 \) is assumed to be equal to the radius of the drop. With these assumptions the pressure difference between the interface of the phases becomes

\[
\Delta P = 2\sigma / d_{sv}
\]

(2)
where \( d_{vs} \) is the diameter of the drop

The pressure difference can be also calculated, at the point of drop break-off, by hydrostatic pressure

\[
\Delta P = (\rho_c - \rho_d) g H
\]  

(3)

where \( \rho_c \) is the density of the continuous phase

\( \rho_d \) is the density of the dispersed phase

\( H \) is the total length of the drop

The total length of the drop

\[
H = (3/2)d_{vs}
\]  

(4)

can be observed in Figure 4 when it is assumed that \( V_1 = V_2 \) and \( h = d_{vs} \).

When Equations (1), (2), (3) and (4) are combined, an equation for the drop size is formed:

\[
d_{vs} = 1.15 \eta \left[ \frac{\sigma}{\Delta \rho g} \right]^{0.5}
\]  

(5)

where \( \eta \) is a correction factor

The correction factor is calculated from the experimental data and it is assumed to be 1.0 when mass transfer is negligible or when mass transfer is from the continuous to the dispersed phase. When mass transfer is from dispersed to continuous phase the correction factor is 1.0-1.8. [2]

4.12 Drop hydraulic and phase velocities

When the efficiency and capacity of a liquid-liquid extraction column is considered, the single most important variable is the drop movement. The movement is based on drag and buoyancy forces. The net buoyant force can be determined by Archimedes’ law. [2] Drops move through the continuous phase of the column driven by the density difference as follows [5]
\[ F_b = gV_d(\rho_c - \rho_d) \]  \hfill (6)

where \( V_d \) is the volume of the drop

The drag force is determined by the drag equation of fluid dynamics

\[ F_d = \frac{1}{2} C_d \rho_c A_{pr} U_{so}^2 \]  \hfill (7)

where \( C_d \) is the drag coefficient

\( A_{pr} \) is the project area of the sphere

\( U_{so} \) is the slip velocity at low dispersed phase flow rate

An initial assumption is that the single drop moves its terminal velocity in an un-packed column. This assumption is corrected later for packed columns. For un-packed columns an overall force balance becomes

\[ F_b - F_d = 0 \]  \hfill (8)

When Equations (6) and (7) are placed into Equation (8), the low dispersed phase rate (at low dispersed phase holdup) can be determined by Equation (9), provided that the drop is assumed to be spherical.

\[ U_{so} = \left[ \frac{4\Delta \rho g d_{vs}}{3\rho_c C_d} \right]^{0.5} \]  \hfill (9)

Equation (9) is corrected by a function \( f(\phi_d) \) in which \( \phi_d \) is the fraction of volume occupied by the dispersed phase, dispersed phase holdup. That function, determined later, accounts for drop-drop interactions. A new equation for slip velocity at higher holdup can be estimated with that function. [2]

\[ U_s = U_{so} f(\phi_d) \]  \hfill (10)

It is assumed that the phases stream toward each other as layers. When the continuous phase flows toward the drops, the drop velocity is decreased. At the same time dispersed phase holdup increases if the flow rate of dispersed phase is maintained. That is why the remaining flow area for the flow of the continuous phase
gets narrower. [5] Thus, the interstitial velocity of the continuous phase is determined by an equation:

\[ U_{ic} = \frac{U_c}{\varepsilon(1 - \phi_d)} \]  

(11)

It is a function of superficial continuous phase velocity \( U_c \), packing void fraction \( \varepsilon \) and the void volume occupied by the dispersed phase \( \phi_d \). [2]

When the velocity of the dispersed phase and interstitial velocity of the continuous phase are combined, the relative slip velocity is formed.

\[ U_s = U_t + U_{ic} \]  

(12)

where \( U_t \) is the velocity of the drop

\( U_{ic} \) is the interstitial velocity of the continuous phase

When Equations (10) and (11) are combined, the velocity of the drop is:

\[ U_t = U_{so} f(\phi_d) - U_{ic} \]  

(13)

This model is suitable for spray columns when packings are not present. Packed columns need more correction factors, which are determined next. [2]

4.13 Corrections for drop movement

The packing and the presence of other drops increase the path traveled by a drop. The total restricting movement, caused by the packing and other drops can be determined as follows

\[ a = a_s + a_p \]  

(14)

where \( a_s \) is the liquid-liquid interfacial area due to static holdup

\( a_p \) is the specific packing surface

The specific packing surface \( a_p \) is a variable which determines the total packing surface area per unit volume of empty column and it depends on the packing ma-
terial. The liquid-liquid interfacial area \( a_s \) is the mass transfer area between the phases due to static holdup. [2]

\[
a_s = 6 \phi_s / d_{vs}
\]

(15)

where \( \phi_s \) is an empirical correlation for static holdup

The empirical correlation is determined by an equation

\[
\phi_s = 0.076 \alpha_p d_{vs}
\]

(16)

The empirical correlation is used when transferring a solute from the continuous water phase to the dispersed organic phase. The correlation is negligible when the direction of the transferring is from the dispersed phase to the continuous phase. [2]

The path of a drop can be approximated by aid of the total surface restricting movement of the drop \( a_d \), which was determined in Equation (14). The tortuous factor

\[
\zeta = a d_{vs} / 2
\]

(17)

estimates the tortuous path of the drop. [2]

The tortuous path of the drop has an impact on the drop and slip velocities. It is assumed that the velocity of the drop varies with the angle of ascent

\[
\theta_a = \frac{\pi}{2} - \frac{\pi \zeta}{4}
\]

(18)

which can be seen in Figure 5. [2]
Thus, the velocity of the drop can be determined again with Equation (13), the angle \( \frac{\pi \zeta}{4} \) and the tortuous factor.

\[
U_t = (U_{so} f\{\phi_d\} - U_{ic}) \cos\left(\frac{\pi \zeta}{4}\right)
\]  

(18)

The slip velocity of the dispersed phase can be formed again by combining Equations (12) and (18).

\[
U_s = U_{so} f\{\phi_d\} \cos\left(\frac{\pi \zeta}{4}\right) + [1 - \cos\left(\frac{\pi \zeta}{4}\right)] U_{ic}
\]  

(19)

The distance of the drop path is introduced in an equation

\[
S = Z \left[ \cos\left(\frac{\pi \zeta}{4}\right) \right]^{-1}
\]  

(20)

where \( Z \) is the vertical path of the drop.
4.14 Dispersed phase holdup

The volume fraction of the dispersed phase (holdup) within the column is defined as

\[
\phi_d = \frac{N_{dr} \pi d_{dr}^3}{6 \varepsilon A_c Z}
\]  

(21)

where \( N_{dr} \) is the number of drops in the contacting section and \( A_c \) is the cross-sectional area of the column.

The equation is formed when the dispersed phase volume is divided by the total contacting volume of the column. The number of drops can be evaluated by an equation

\[
N_{dr} = \left( \frac{6Q_d (t_{dr})}{\pi d_{dr}^3} \right)
\]  

(22)

where \( t_{dr} \) is the drop residence time and \( Q_d \) is dispersed phase flow rate.

The drop residence time is based on an equation

\[
t_{dr} = S / U_t
\]  

(23)

When Equations (20) and (18) are placed into Equation (23), the residence time is:

\[
t_{dr} = \frac{Z}{(U_{so} f \{ \phi_d \} - U_{ic} \left[ \cos \left( \frac{\pi \phi_{ic}}{4} \right) \right] t_{dr}}
\]  

(24)

Now this equation can be placed into Equation (22).
A new equation for the dispersed phase holdup is formed when Equation (25) is placed into Equation (21)

\[
\phi_d = \frac{Q_d}{\varepsilon A_c (U_{so} f \{\phi_d\} - U_w) \left[ \cos \left( \frac{\pi \varepsilon}{4} \right) \right]^2}
\]  

Equation (26) is reduced to the form

\[
\phi_d = \frac{U_d \cos \left( \frac{\pi \varepsilon}{4} \right)^2}{\varepsilon (U_{so} f \{\phi_d\} - U_w)}
\]  

From where \( \phi_d \) is solved by iteration and

where \( U_d \) is the dispersed phase slip velocity

With dispersed phase holdup the interfacial area between liquids can be determined again

\[
a_d = \frac{6\alpha \phi_d}{d_{vs}}
\]  

4.15 Flooding

The flooding point of the counter-current column is reached when the flow rates of the column are the highest possible and no further increase of the flow rates can be performed by the density difference. At the flooding point the light phase
leaves the column at the bottom instead of at the top and the heavy phase conversely. [5]

The dispersed phase holdup gets a maximum value at the flooding point and then the increase of the flow rate cannot increase the drop holdup [2,5]. It is assumed that dispersed phase travels in spherical droplets and the droplets are placed inside of cubes. Then the volume of the cubes is $d_{vs}^3$. Thus the maximum dispersed phase holdup is:

$$\phi_{d,\text{max}} = \frac{\pi}{6}$$  \hspace{1cm} (29)

At the flooding point an increase of the flow rate cannot increase the drop holdup [5]. Then an equation

$$\left. \frac{\partial U_d}{\partial \phi_d} \right|_{u_c} = \left. \frac{\partial U_c}{\partial \phi_d} \right|_{u_d} = 0$$  \hspace{1cm} (30)

is obtained. That equation can be solved by differentiating Equation (27). The continuous velocity term is assumed to be negligible. The differentiated equation is

$$\phi_d f'(\phi_d) + f\{\phi_d\} = 0$$  \hspace{1cm} (31)

and at the flooding point the dispersed phase holdup gets the maximum value, $\phi_d = \pi / 6$.

Now the drop-drop interaction function $f\{\phi_d\}$ is obtained by solving the differential Equation (31)

$$f\{\phi_d\} = \exp(-6\phi_d / \pi)$$  \hspace{1cm} (32)

Equation (31) can be placed into Equations (18), (19) and (27). Then the new equations are
\[ U_t = (U_{so} \exp(-6\phi_d / \pi) - U_{ic}) \cos\left(\frac{\pi \xi}{4}\right) \]  
(33)

\[ U_s = U_{so} \exp(-6\phi_d / \pi) \cos\left(\frac{\pi \xi}{4}\right) + \left[1 - \cos\left(\frac{\pi \xi}{4}\right)\right]U_{ic} \]  
(34)

\[ \phi_d = \frac{U_d \left[\cos\left(\frac{\pi \xi}{4}\right)\right]^2}{\varepsilon(U_{so} \exp(-6\phi_d / \pi) - U_{ic})} \]  
(35)

Continuous phase flooding velocity \( U_{cf} \) can be determined by aid of Equation (35). When Equations (11) and (29) are placed into Equation (35), equation

\[ \frac{U_{cf}}{6} - 1 = \frac{1}{\pi} \left[\cos\left(\frac{\pi \xi}{4}\right)\right]^2 U_{df} = \frac{\pi}{6} \varepsilon U_{so} \exp(-1) \]  
(36)

where \( U_{df} \) is the dispersed phase flooding velocity is formed. The above equation is reduced to the forms:

\[ 1.08U_{cf} + \left[\cos\left(\frac{\pi \xi}{4}\right)\right]^2 U_{df} = 0.192 \varepsilon U_{so} \]  
(37)

\[ \frac{1}{U_{cf}} = \frac{5.63}{\varepsilon U_{so}} + \frac{5.21}{\varepsilon U_{so}} \left[\cos\left(\frac{\pi \xi}{4}\right)\right]^2 \frac{U_{df}}{U_{cf}} \]  
(38)

In Equation (38), the ratio of the flooding velocities \( \frac{U_{df}}{U_{cf}} \) is defined as \( d_{fr} \). Now, the continuous phase flooding velocity can be calculated by equation:

\[ U_{cf} = 0.1776 \varepsilon U_{so} + 0.1919 \varepsilon U_{so} \left[\cos\left(\frac{\pi \xi}{4}\right)\right]^2 \frac{1}{d_{fr}} \]  
(39)

With the flooding velocity it is possible to calculate the required cross-sectional area of the column

\[ A_c = \frac{Q_c}{U_{cf}} \]  
(40)
where \( Q_c \) is the continuous phase flow rate.

### 4.16 Mass Transfer

When the raffinate and the extract phase are in contact with each other the mass transfers from raffinate into the extract, as it was described previously. The mass transfer efficiency depends on the concentrations of the transitional component in the phases and mass transfer resistances (mass transfer coefficients). [1] Thus, the mass transfer fluxes between two phases can be determined by equations

\[
N_c = K_{oc} (c_c - c'_c) \quad (41)
\]

\[
N_d = K_{od} (c'_d - c_d) \quad (42)
\]

where

- \( N_c \) is the mole flux of the transitional component in the continuous phase
- \( N_d \) is the mole flux of the transitional component in the dispersed phase
- \( K_{oc} \) is the overall mass transfer coefficient based on the continuous phase
- \( K_{od} \) is the overall mass transfer coefficient based on the dispersed phase
- \( c \) is the concentration of the bulk phase
- \( c'_c \) is the equilibrium concentration of the phase

The overall mass-transfer coefficients \( K_{oc} \) and \( K_{od} \) are determined from the two film resistance theory by equations:

\[
\frac{1}{K_{oc}} = \frac{1}{k_c} + \frac{1}{m_{dc} k_d} \quad (43)
\]

\[
\frac{1}{K_{od}} = \frac{1}{k_d} + \frac{m_{dc}}{k_c} \quad (44)
\]

where \( k_c \) is the mass-transfer coefficient based on the continuous phase.
\[ k_d \] is the mass-transfer coefficient based on the dispersed phase

\[ m_{dc} \] is the distribution coefficient based on a concentration driving force

\[ m_{dc}^{''} \] is the distribution coefficient based on a concentration driving force

In the design of extraction columns, which include complex flows, the mass-transfer coefficients are determined by experiments, as Seibert and Fair have done. After that, the coefficients are correlated, for example, with system properties and molecular diffusivity [1].

The continuous phase mass-transfer coefficient is determined by an equation

\[ k_c = Sh_c \left( \frac{D_c}{d_{vs}} \right) \]  

where \( Sh_c \) is Sherwood number based on the continuous phase

\[ D_c \] is the diffusion coefficient of the continuous phase

The Sherwood number is approximated by an equation

\[ Sh_c = 0.698 S_c^{0.4} Re_c^{0.5} \left( 1 - \phi_d \right) \]  

where \( S_c \) is Schmidt number based on the continuous phase

\[ Re_c \] is Reynolds number based on the continuous phase

The Schmidt and Reynolds number are defined as follows:

\[ S_c = \frac{\mu_c}{\rho_c / D_c} \]  

where \( \mu_c \) is the viscosity of the continuous phase

\[ Re_c = \frac{\rho_c U_c d_{vs}}{\mu_c} \]  

There are two calculating methods for the disperse phase coefficient in Seibert’s and Fair’s research. The first method does not involve diffusion and it is introduced by an equation
\[ k_d = 0.00375 \cdot U_s/(1 + \mu_d / \mu_i) \]  \hspace{1cm} (49)

where \( \mu_d \) is the viscosity of the dispersed phase

The second method permits consideration of molecular diffusion:

\[ k_d = 0.023 \cdot U_s/(Sc_d)^{-0.5} \]  \hspace{1cm} (50)

where \( Sc_d \) is Schmidt number based on the dispersed phase

It depends on the hydrodynamics conditions, which method is used. Seibert and Fair have used a parameter

\[ \Phi = (Sc_d)^{-0.5} \cdot (1 + \mu_d / \mu_i) \]  \hspace{1cm} (51)

as a criterion of choice. When \( \Phi < 6 \), equation (49) is used and when \( \Phi > 6 \), equation (50) is used.

The overall mass transfer coefficient of the raffinate phase is used in the column design calculation. The definition of the mass transfer unit follows from the mass transfer equation. With a differential mass balance and the mass transfer flux, the following equation is formed

\[ -Q_c dc = K_{oc} a_i (c - c^*) A_i dz \]  \hspace{1cm} (52)

where \( Q_c \) is the continuous phase flow rate

\( K_{oc} a_i \) is the volumetric mass transfer coefficient

\( dc \) is the concentration difference of the dissolved component

\( dz \) is the column height difference

from which the required contacting height of the column can be approximated. Equation (52) can be integrated and the following equation is obtained

\[ z = \frac{-Q_c}{K_{oc} a_i A_c} \int_0^z \frac{dc}{c - c^*} \]  \hspace{1cm} (53)
\[ z = \frac{U_c}{K_{oc} a_i} \int_0^Z \frac{dc}{c - c_i} \]  

(54)

\[ z = HTU_{oc} NTU_{oc} \]  

(55)

where \( HTU_{oc} \) is the height of transfer unit
\( NTU_{oc} \) is the number of transfer units

The height of the column can be approximated with the transfer units. In the applied part of this work the height of the column is calculated by simulation and transfer units. These results are presented in the column design case section.

5 SIMULATION AND DESIGN OF EXTRACTION COLUMN

A counter current packed liquid-liquid extraction column is simulated and designed in this part. The aim was to simulate and design a column, which separates carboxylic acid from aqueous phase to an organic solvent phase when the flow rates and the extraction yield is known. The solution-solvent system consists of formic acid, n.n-dibutylformamide and water. The equilibrium curve of this system is determined by an equation:

\[ y = 0.6252x^{0.6594} \]  

(56)

where \( y \) is the formic acid mass fraction in aqueous phase
\( x \) is the formic acid mass fraction in organic phase

Equation (56) is based on the equilibrium data of formic acid between aqueous and organic phase and it is given in mass fractions. The material properties of the formic acid-n.n-dibutylformamide-water system are given in Table I.

<table>
<thead>
<tr>
<th>Material qualities of the solution-solvent system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
</tr>
<tr>
<td>Molar mass, [kg/mol]</td>
</tr>
<tr>
<td>Density, [kg/m³]</td>
</tr>
<tr>
<td>Viscosity, [kg/sm]</td>
</tr>
</tbody>
</table>
The column works at 60 % of the flooding velocity at 25 °C and normal pressure. The aqueous phase is continuous and the organic dispersed. The heavy aqueous liquid is fed at the top of the column and the light solvent at the bottom. The basic operational conditions and quantities can be seen in Table II.

Three simulation and design cases were done with different solution-solvent ratios with 95 % extraction yield. The solution-solvent ratios were (1:1), (1:2) and (1:3).

Table II Basic specifications of the simulation and design cases

<table>
<thead>
<tr>
<th></th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{aq} ), [m³/h]</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>( V_{solv} ), [m³/h]</td>
<td>30</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>( V_{aq} / V_{solv} ), [-]</td>
<td>1:1</td>
<td>1:2</td>
<td>1:3</td>
</tr>
<tr>
<td>Mass fraction of the acid in the feed aqueous flow, [-]</td>
<td>0.035</td>
<td>0.035</td>
<td>0.035</td>
</tr>
<tr>
<td>Mass fraction of the acid in the feed solvent flow, [-]</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Extraction yield, [%]</td>
<td>95</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>( U_c ), [m/s]</td>
<td>( 0.6U_{cf} )</td>
<td>( 0.6U_{cf} )</td>
<td>( 0.6U_{cf} )</td>
</tr>
<tr>
<td>( C_D ), [-]</td>
<td>0.55</td>
<td>0.55</td>
<td>0.55</td>
</tr>
<tr>
<td>( \alpha_p ), [m²/m³]</td>
<td>205</td>
<td>205</td>
<td>205</td>
</tr>
<tr>
<td>( \sigma ), [N/m]</td>
<td>( 22 \cdot 10^3 )</td>
<td>( 22 \cdot 10^3 )</td>
<td>( 22 \cdot 10^3 )</td>
</tr>
<tr>
<td>( \varepsilon ), [-]</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
</tbody>
</table>

5.2 Numerical methods of lines

The mass balance equations of the simulation column, which are introduced later in this work, are partial differential equations, (PDEs). The equations provide a mathematical description of physical three-dimensional spacetime. [7] In the simulation column the acid molar flow in liquid-phases is described when time and space varies and that is the spacetime in the column case. Both phases (continuous and dispersed) need own balance equation. Each of them includes two independent variables (space and time) and one dependent variable (concentration of the acid). [7]
Before the solutions for these PDEs can be calculated, some auxiliary conditions must be determined. These auxiliary conditions are initial and boundary conditions. Each phase of the column needs one initial value and two boundary values. [7] The initial values \( t = 0 \) for the balance equations are known and they are the entrance concentrations of the acid. The boundary values for the equations are first order space derivatives of the acid concentration. The boundary values are determined at the bottom and at the top of the column \( z = [0, L] \). These boundary values are called Neumann boundary values.

The PDEs, are solved by numerical methods of lines, (NUMOL). It is a numerical procedure in which the spatial partial derivatives of the PDEs are approximated numerically, in this work by finite differences. The MOL approximation replaces the PDE system with ODE (ordinary differential equation) system. As a result, a system of ODEs is obtained which approximate the original PDEs. [7] The solution of ODE-system can be calculated by integration, for example with ODE-integrator of MATLAB.

### 5.1 Mass balances of the simulated column

One of the most used models for continuous counter current extraction column is the axial dispersion model and it is also used in this work. The axial dispersion implies phase mixing in axial direction and the dispersion of residence time of the continuous and dispersed phase. The dispersion process is considered to be in analogy to Fick’s law of molecular diffusion: [5]

\[
R = -D_{ax} A_c \frac{dc}{dz}
\]

(57)

where \( D_{ax} \) is the axial dispersion coefficient

\( R \) is the dispersion rate

However, in this work the model is used without axial dispersion due to insignificant axial dispersion in packed columns as investigated by Seibert and Fair.

The total molar flow rate of the dissolved component consists of an axial convection flow, axial dispersion flow and mass transfer flow between two phases. The
balance of the dissolved component leads to second-order partial differential equations for both two phases. The balance equations are: \[5\]

\[
\frac{\partial c_c}{\partial t} = U_c \frac{\partial c_c}{\partial z} + D_{ax,c} \frac{\partial^2 c_c}{\partial z^2} - N_c a_i
\] (58)

\[
\frac{\partial c_d}{\partial t} = -U_d \frac{\partial c_d}{\partial z} + D_{ax,d} \frac{\partial^2 c_d}{\partial z^2} + N_d a_i
\] (59)

These balance equations can be also presented by molar flows instead of concentrations:

\[
\frac{\partial n_c}{\partial t} = U_c \frac{\partial n_c}{\partial z} + D_{ax,c} \frac{\partial^2 n_c}{\partial z^2} - N_c a_i U_c A_c
\] (60)

\[
\frac{\partial n_d}{\partial t} = -U_d \frac{\partial n_d}{\partial z} + D_{ax,d} \frac{\partial^2 n_d}{\partial z^2} + N_d a_i U_d A_c
\] (61)

### 5.2 Solution of the mass balances

The partial differential equations can be solved for special initial and boundary conditions. The initial values are known at the beginning of the extraction operation \(t = 0\). Then the entrance concentrations of the acid are known in the dispersed and in the continuous phase. The boundary conditions are known at the top and at the bottom of the column \((z = L)\), \((z = 0)\).

The initial values for the balance equations are

for \(t = 0\)

\[
c_c = c_{c,E}
\] (62)

\[
c_d = c_{d,E}
\] (63)

where subscript \(E\) refers to an entrance concentration of the column.

The Neumann boundary conditions for the column, when the organic phase is dispersed, are
for \( z = 0 \)

\[
\frac{\partial c_c}{\partial z} = 0
\]  

(64)

\[
\frac{\partial c_d}{\partial z} = \frac{U_d (c_{d,1} - c_{d,E})}{D_{ax}}
\]  

(65)

where the subscript 1 refers to the first discrete section of the column.

for \( z = L \)

\[
\frac{\partial c_c}{\partial z} = \frac{U_c (c_{c,E} - c_{c,L})}{D_{ax}}
\]  

(66)

where the subscript L refers to the last discrete section of the column.

\[
\frac{\partial c_d}{\partial z} = 0
\]  

(67)

5.3 Simulation program

The coupled partial differential equation system can be solved by the numerical methods of lines with MATLAB. The Simulation program was developed to solve the equation system and the operation principles of it are presented next.

The Simulation program consists of main program and some subprograms. The main program includes the basic variables of the extraction operation. The main program includes an ode-solver, which solves the ordinary differential equations of the subprogram until a steady-state is achieved. The partial differential equations of the column model are converted to ordinary differential equations in the subprogram by the aid of the functions to calculate spatial derivatives. These functions are dss002 and dss042 which are introduced by Schiesser and Griffiths [7]. The first and the second order space derivatives of the acid flow can be approximated with these functions in both phases. The solution of the ordinary differential equations consists of the molar flows of the acid in the solution and in the solvent phase along the column. The initial values for the ode-solver are the
feed molar flows of the liquids, which are determined previously. For the simulation the column is divided to 60 discrete sections and the molar flow of the acid is calculated in each section by simulation.

One of the subprograms includes the hydrodynamic models of the packed extraction column, which are based on Seibert’s and Fair’s research. The used models were represented previously in this work.

The simulation and design are performed by trial and error. It is guessed an initial value for the length of the column. That guess is corrected by aid of the extraction yield. The yield should be 95 %. Thus, the new value of the length is guessed based on the known yield.

5.4 Simulation results

The simulation results of the case 1 are introduced in this part. The mass transfer resistances of this case are also studied.

The simulation results are in Table II. The graphical representation of the results can be seen in Figure 6 in which the acid molar flows are introduced along the column. There is only part of the simulation results in Table II but the results of all 60 column sections are in Figure 6.
Table II  
Simulation results of the case 1. Solution-solvent ratio is (1:1) and the aqueous phase is continuous.

<table>
<thead>
<tr>
<th>n, [-]</th>
<th>z, [m]</th>
<th>Acid in aqueous phase, [mol/s]</th>
<th>Acid in solvent phase, [mol/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.3175</td>
<td>2.6614·10⁻⁵</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>0.4290</td>
<td>0.1172</td>
</tr>
<tr>
<td>10</td>
<td>0.91</td>
<td>0.6178</td>
<td>0.3096</td>
</tr>
<tr>
<td>15</td>
<td>1.41</td>
<td>0.8652</td>
<td>0.5612</td>
</tr>
<tr>
<td>20</td>
<td>1.92</td>
<td>1.1792</td>
<td>0.8797</td>
</tr>
<tr>
<td>25</td>
<td>2.42</td>
<td>1.5660</td>
<td>1.2715</td>
</tr>
<tr>
<td>30</td>
<td>2.92</td>
<td>2.0300</td>
<td>1.7406</td>
</tr>
<tr>
<td>35</td>
<td>3.43</td>
<td>2.5726</td>
<td>2.2883</td>
</tr>
<tr>
<td>40</td>
<td>3.93</td>
<td>3.1926</td>
<td>2.9132</td>
</tr>
<tr>
<td>45</td>
<td>4.44</td>
<td>3.8862</td>
<td>3.6114</td>
</tr>
<tr>
<td>50</td>
<td>4.94</td>
<td>4.6474</td>
<td>4.3767</td>
</tr>
<tr>
<td>55</td>
<td>5.45</td>
<td>5.4686</td>
<td>5.2022</td>
</tr>
<tr>
<td>60</td>
<td>5.95</td>
<td>6.3404</td>
<td>6.0523</td>
</tr>
</tbody>
</table>

Figure 6.  
Graphical representation of the simulation results of the case 1. Solution-solvent ratio is (1:1) and the aqueous phase is continuous.
The solution of the simulation case 1 by methods of lines is illustrated in Figures 7 and 8. The simulation results are represented in three dimensional spacetime in these figures. The acid molar flows in aqueous phase along the column, when time varies, are introduced in Figure 7. The acid molar flows in organic phase can be seen in Figure 8.

Figure 7. Spacetime of acid in aqueous phase. The results are from the simulation case 1. Initial condition: \( n(x,0) = 6.34 \text{ mol/s} \).
Figure 8. Spacetime of acid in organic phase. The results are from the simulation case 1. Initial condition: \( n(x,0) = 0 \text{ mol/s} \).

The mass transfer resistances of the aqueous and the organic phase along the column can be seen in Figure 9.

Figure 9. Mass transfer resistances of the simulation case 1.
The equilibrium of the acid between the organic and aqueous phase is presented by equilibrium curve in Figure 10. The operation line of the column (case 1) can be seen in the same figure. The acid molar fractions can be seen in Figure 11.

Figure 10. Equilibrium curve and operation line of the simulation case 1.

Figure 11. Acid molar fractions of the simulation case 1.
The overall mass transfer coefficient, based on the aqueous phase, is presented in Figure 12. The coefficient is calculated by Equation (43).

![Graph](Image)

**Figure 12.** Overall mass transfer coefficient of the simulation case 1.

### 5.5 Column design case

The results of the column design cases, which are based on the same simulation cases, presented earlier, are introduced in Table III. The height of the column was calculated both by the simulation and by the transfer units.

The extraction yields were simulated for solution-solvent ratios (1:1), (1:2), (1:3) as function of the column height. 23 simulations were done for the case 1, 16 for the case 2 and 13 for the case 3. The results are presented in Figure 13.
Table III The results of the column design cases.

<table>
<thead>
<tr>
<th></th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of the column, [m]</td>
<td>5.95</td>
<td>2.60</td>
<td>1.74</td>
</tr>
<tr>
<td>Diameter of the column, [m]</td>
<td>1.31</td>
<td>1.62</td>
<td>1.87</td>
</tr>
<tr>
<td>Length of the column by HTU and NTU, [m]</td>
<td>9.05</td>
<td>4.52</td>
<td>3.09</td>
</tr>
<tr>
<td>Extracted yield, [%]</td>
<td>95</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>Dispersed phase holdup, [-]</td>
<td>0.0741</td>
<td>0.1004</td>
<td>0.1137</td>
</tr>
<tr>
<td>Acid balance, [%]</td>
<td>-0.46</td>
<td>-2.1</td>
<td>-4.5</td>
</tr>
</tbody>
</table>

Figure 13. Extraction yields with different solution-solvent ratios. The design cases are implied by dashed lines.
6 CONCLUSIONS

Liquid-liquid extraction is a separation method, which is used to recover a valuable or to remove an unwanted product from a solution. It is widely used in processing industry with both batch-wise and continuous equipment. A short review of liquid-liquid extraction with the equipment, such as mixer-settler, spray, packed and sieve-plate columns, was given in this work. The packed spray column was studied in more detail by modeling and simulation.

A counter current packed extraction column was modeled in the applied part of this work. The hydrodynamic models of the column, which base on Seibert’s and Fair’s investigation Hydrodynamics and Mass Transfer in Spray and Packed Liquid-Liquid Extraction Columns, were introduced. These models were used in the computer code which was used to simulate and design the column. The column was simulated by Numerical Method of Lines and the principles of this method were presented.

The counter current packed extraction column was simulated with three solution-solvent ratios (1:1), (1:2) and (1:3) in which extraction yield was 95 %. The results of the case 1 (1:1) were studied in more detail and they were presented in Table II and in Figure 6. The results implied the acid molar flow in the aqueous and organic phases along the column. The material balance of the acid was -0.46 % for the case 1 and this was the best accuracy which was calculated by the simulation program. The balances for the other cases were -2.1 % (case 2) and -4.5 %, (case 3). The simulation program provided a good accuracy when solution solvent ratio was (1:1). The results of the acid balance imply that the development of the program is needed so that more qualified results are achieved.

The mass transfer resistances of the case 1 were studied in Figure 9. The results show that the major resistance, along the column, is in the aqueous phase and this resistance is a constant. The resistance of the organic phase increases through the column and it crosses the resistance of the aqueous phase when the height of the column is 5.5 m. The variation of the organic phase resistance results from the slope of the equilibrium curve, which decreases when the acid mole fraction in the organic phase increases. This can be seen in Figure 10. The acid mole fraction of
the organic phase is low at the bottom of the column as can be seen in Figure 11. That’s why the resistance is low and the mass transfer efficient. The resistance increases when the acid mole fraction of the organic phase increases towards the top.

The overall mass transfer coefficient, based on the aqueous phase, was presented in Figure 12. The mass transfer coefficient decreases when the height of the column increases. Consequently, the mass transfer efficiency decreases towards the top of the column.

The height of the column was approximated by simulation and by transfer units with three solution-solvent ratios (1:1), (1:2), (1:3). Desired extraction yield was 95 %. The design results by simulation were 6.0 m, 2.6 m, 1.8 m and these results can be seen in Figure 13 and in Table III. The results of transfer units were 9.1 m, 4.5 m, 3.1 m.

Both results imply, how the necessary height of the column decreases when the solution-solvent ratio decreases (solvent flow rate increases). Thus, the mass transfer that is needed, for example for 95 % extraction yield, is achieved by a lower column if solvent flow rate is higher. The reason for this is the dispersed phase holdup which increases when the solvent flow rate increases. The results of the dispersed phase holdup are in Table III. When dispersed phase holdup is high, the interfacial area of the phases is wide and the mass transfer is efficient.

The approximation of column height with transfer units is not as accurate as the approximation by simulation since both $HTU_{oc}$ and $NTU_{oc}$ must be approximated. The height of the transfer unit is calculated with overall mass transfer coefficient which is a mean value of the column and this is a cause of the inaccuracy. Besides the number of the transfer units is calculated by integral approximation and this also increases inaccuracy.
LITERATURE


