6 TOOL FOR THE SIMULATION : GETTING STARTED

It is evident that all mass transfer approaches are based on the same physicochemical behaviour:

- solvent diffusion through the internal volume of the sample
- diffusion of the product through the surface boundary layer
- surface desorption of the product of interest
- transport from the surface into the bulk supercritical fluid phase

A simulation algorithm may be designed as follows:

1. The necessary parameters for the simulation may consequently be catalogised:

<table>
<thead>
<tr>
<th>Molecular properties</th>
<th>Batch</th>
<th>Process parameters</th>
<th>Fluid parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar weight</td>
<td>shape</td>
<td>pressure</td>
<td>Fluid direction</td>
</tr>
<tr>
<td>Molar diameter</td>
<td>porosity</td>
<td>temperature</td>
<td>Initial concentration</td>
</tr>
<tr>
<td>Norm viscosity</td>
<td>Particle surface</td>
<td>Column length</td>
<td>Mass flow</td>
</tr>
<tr>
<td>Norm binary diffusivity</td>
<td>Initial concentration</td>
<td>Column diameter</td>
<td></td>
</tr>
<tr>
<td>Norm density</td>
<td>Tortuosity</td>
<td>diameter</td>
<td></td>
</tr>
</tbody>
</table>

*Table 6.1: necessary information for simulation of a Batch SFE process*

2. With this data set, the subsequent estimation of physico-chemical parameters is feasible

<table>
<thead>
<tr>
<th>Properties</th>
<th>Fluid Dynamics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid density</td>
<td>Reynolds Number</td>
</tr>
<tr>
<td>Fluid viscosity</td>
<td>Axial Dispersion and Peclet numbers</td>
</tr>
<tr>
<td>Binary diffusion coefficient</td>
<td>1st approach Sherwood number</td>
</tr>
<tr>
<td>1st approach effective diffusion coefficient</td>
<td>Mass transfer coefficient</td>
</tr>
<tr>
<td>Schmidt number</td>
<td>Biot number</td>
</tr>
</tbody>
</table>

*Table 6.2: Calculated information*

3. Additional profit can be taken from the shape of the experimental curve, i.e. the visual definition of the interacting region between constant extraction rate and the falling extraction rate. From the information on the so-called “operational solubility” a first guess on diffusion effects (solid phase, effective, or wet phase) is feasible.

The simulation can be optimised for the

- Diffusion-Desorption-Dispersion Model by simply adapting the desorption equilibrium coefficient
- Shrinking core model by adapting the Biot number
- Sovova model without any additional modification
6.1 Algorithm

The simulation of the equation system will require a computer-supported solver of ordinary differential equations, due to the structure of the mass balance in discrete equilibrium cells. Number of equilibrium cells can be calculated according axial dispersion (Bo) and thus NTh number.

Consider the mass balance

\[
\text{Input} - \text{Output} = \text{Accumulation}
\]

in one equilibrium cell \( i \), where the component of interest is distributed in solid phase (concentration \( c^{II}_{i} \)), and fluid phase (concentration \( c^{I}_{i} \)).

For the desorption/diffusion/dispersion model one may discretise

\[
\frac{\varepsilon \cdot V}{NTh} \cdot \rho_{CO2} \cdot \frac{\partial c^{I}_{i}}{\partial t} = \dot{V} \cdot \rho_{CO2} \cdot c^{I}_{i-1} + \dot{m}_{\text{Desorption}} - \dot{\rho}_{CO2} \cdot c^{I}_{i} \quad (6.1)
\]

\[
\frac{(1 - \varepsilon) \cdot V}{NTh} \cdot \rho_{\text{solid}} \cdot \frac{\partial c^{II}_{i}}{\partial t} = -\dot{m}_{\text{Desorption}} \quad (6.2)
\]

with \( \rho_{\text{solid}} \) referring to true density = \( \rho_{\text{bulk}}/(1-\varepsilon) \)

The other models use an analogous approach, e.g. instead of the solid concentration, Goto model defines the front of the shrinking core in the second equation.

In the case of more complex models (e.g. Reverchon et al.) a third equation describes either the negative accumulation of the free accessible solute, or the shrinking core for non-spherical particles.

Concentrations can be isolated on the right side of the equation:

\[
t_{0} \cdot \frac{\partial c^{I}_{i}}{\partial t} = (c^{I}_{i-1} - c^{I}_{i}) + \frac{\dot{m}_{\text{Desorption}}}{V \cdot \rho_{\text{fluid}}} \quad (6.3, 6.4)
\]

The desorption term itself describes the diffusional/desorptional mass flow due to the concentration profile \( c_{\text{solid}}^*K - c_{\text{fluid}} \), depending on the adsorptive equilibrium between solid and fluid phase:

Desorption terms are given by

\[
\dot{m}_{\text{Desorption}} = (c^{I}_{i} - c^{II}_{i} \cdot K) \cdot a_{\text{spec}} \cdot k_{\text{aG}} \cdot \varepsilon \cdot V / NTh \cdot \rho_{\text{fluid}} \quad (6.5)
\]

with respect to the different mass concentration of the compound relative solid and fluid phase (porosity/density).
At \( t = 0 \), concentration on solid and fluid phase is given by the initial value

\[
\begin{align*}
    c^{II} (t = 0) &= \frac{\text{total extractable mass}}{\text{raw material mass input}} \\
    c^I (t = 0) &= 0, \\
\end{align*}
\]

for all plates from \( i = 1 \ldots \text{Nth} \).

\( c^{II} \) is the external input parameter as described in chapter 3.5, whereas care should be taken on the origin of the data (Soxhlet, Steam distillation, maximum SFE yield).

For each time step \( \Delta t \) (\( t = 0 \ldots \text{runtime} \)), the solver may now define a matrix with \( \text{Nth} \) columns and “\( \text{NTh} \times 2 \)” lines (one line for fluid phase concentration and solid phase concentration, respectively);

\[
\begin{bmatrix}
    \frac{\partial c^I}{\partial t} \\
    \frac{\partial c^{II}}{\partial t} \\
    \vdots \\
    \frac{\partial c^I}{\partial t} \\
    \frac{\partial c^{II}}{\partial t} \\
    \vdots \\
    \frac{\partial c^I}{\partial t} \\
    \frac{\partial c^{II}}{\partial t} \\
    \vdots \\
    \frac{\partial c^I}{\partial t} \\
    \frac{\partial c^{II}}{\partial t} \\
   \end{bmatrix}
\]

\[
\begin{pmatrix}
    c_i^I - c_i^{II} \\
    -t_{\text{o}}(c_i^I - c_i^{II}) \cdot \text{desorption} \\
    c_i^I \\
    + (c_i^I - c_i^{II}) \cdot \text{desorption} \\
    c_i^I - c_i^{II} \\
    -t_{\text{o}}(c_i^I - c_i^{II}) \cdot \text{desorption} \\
    c_i^I \\
    + (c_i^I - c_i^{II}) \cdot \text{desorption} \\
    c_{i+1}^I - c_i^I \\
    -t_{\text{o}}(c_{i+1}^I - c_i^{II}) \cdot \text{desorption} \\
    c_i^I \\
    + (c_i^I - c_i^{II}) \cdot \text{desorption} \\
    c_{\text{NTU} - i}^I - c_{\text{NTU}}^I \\
    -t_{\text{o}}(c_{\text{NTU} - i}^I - c_{\text{NTU}}^{II}) \cdot \text{desorption} \\
    c_{\text{NTU}}^I \\
    + (c_{\text{NTU}}^I - c_{\text{NTU}}^{II}) \cdot \text{desorption} \\
\end{pmatrix}
\]

equivalent to the form

\[
\begin{align*}
    A \cdot \frac{\partial c}{\partial t} &= B \\
\end{align*}
\] (6.6)

For a given time step from \( t \) to \( t + \Delta t \), the Livermore solver allows stable iterations in order to obtain the concentration profile of the fluid phase and the solid phase as output. The “GEAR” algorithm allows even the handling of “stiff” equations (e.g. for sharp profile interfaces), which makes the solver to an adapted tool for modelling of combined unit operations (e.g. SFE + SFC, SFE + conversion, SMB, TMB etc.)

Size of Matrix \( A \) increases potentially with \( \text{NTh} \) and number of concentrations, leading to the following problems:

- run time
- stack of variables, especially in the case of multicomponent mixtures (not the case here, but as option for chromatographic separations).

The required stack size for variables of matrix \( A \) can be sufficiently reduced by the pointer method, taking into account that only in the surrounding of the matrix diagonal the variables differ from zero. Therefore, only these variables will be indexed for stock.
The transcription of A-matrix variable positions to pointer positions is given in the following matrix.

\[
A \left( j_{\text{mel}} = \text{equilibrium plate } 1..\text{NTU} , \; i_{\text{esp}} = \text{compound }/\text{phase } I \text{ or } II \right) \rightarrow a^\text{(I pointer queue)} \\
\left( j_{\text{mel}} - 1 \right) \times 2 + i_{\text{esp}} = I
\]

(45)

By means of I, the multiplication term for compound concentration and its plate position is thus completely defined.

However, this formula is only useful in the very specific case that all relevant matrix data are situated in the limited area of ONE position on the right and ONE position below the diagonal \((m_\text{up}=1 , \; m_\text{low}=1)\). More complex systems require a different calculation.

The calculation will be started with the following program lines, to be found in the program unit INTEG.PAS:

```
Init LSO;
Initial;
With LSOD do istate := 0;
DRV_LSODI
```

The program unit PROC_LSO.PAS contains the subroutine DRV_LSODI with the central matrix calculation function

```
Lsodi (NeqUtil, y^, t, tout,…..,mf) \\
Print (t),
```

which calculates the complete concentration profil \(y^\text{(I)}\) of \(c_{\text{fluid}}\) and \(c_{\text{solid}}\) at each position 1..NTh in function of a user defined time step t.
6.2 Getting Started

By means of the Delphi 6.0 programming language, a user friendly tool has been established in 2004-2007, which allows the simulation of the experimental curves in a windows environment. The program can still be modified and is open for different appendencies concerning the calculation model and the input/output environment.

When opening the Program executive file “BatchSFE.exe” the opening window proposes different scroll-down menus, whereas it is usually recommended to follow the methodology from left/top to right/down.

The different forms consist of
- Edit and information windows
- Scroll down menus
- Radio or Check- boxes
- Action Buttons

When changing the values in the Edit windows, care should be taken on the right format (scientific mode or conventional digit mode). The number of digits and the position of the digit point is fixed, missing characters shall be filled with zero.

The choice of options in the scroll down menu, as well as radio- and check boxes will either
- specify subsequent actions of simulation
- specify the information for the output protocol,
- directly start a calculation routine.

In each form, different buttons allow to re-calculate all data referring to the new input, to cancel, to save, and to close and the actions. When pushing the “OK” button, the actualised parameters will be stacked and may be called from the other forms, resp.procedures.

It is therefore strongly recommended to follow strictly the tool bar procedure from left to right, including the scroll down menus from top to bottom.

![Figure 6.1: Opening window, and suggested methodology](image)
6.2.1 File handling

The first scroll down menu considers the file handling.

![Figure 6.2: Creating a new file, or opening an existing one](image)

The scroll down menu “File” [1] provides the option either to create a new file or to open an existing one. When creating a new file, a sub-form will be appear at position [2] which asks for some additional information allowing to identify the file more easily. A check-box in this form can be activated which allows an overwriting of this information at a later status. The new file contains pre-defined data for the modelling, which can be changed individually.

Alternatively an existing file can be opened and modified.

It is recommended to save the data periodically during the session. The appendix of the data files is “.vtx”.
6.2.2 Data Preparation

The modelling session shall be continued with the forms from the scroll down menu “Data Preparation” [1], in which the options “Molecular Properties”, “Batch”, “Process Parameters” and “Column Design” are handled.

A. Molecular Properties

![Molecular Properties Form](image)

**Figure 6.3: Molecular Properties Form**

In this form the specific physicochemical properties of solvent and solute may be entered into the different edit or scroll-down windows.

The upper frame part [2] defines solvent and solute. Solvent name can be chosen between CO₂, Propane, and others. Depending on the choice, the subsequent edit windows in the frame region [3] \((T_c, P_c, V_c, M)\) concerning the solvent data will change their value. The user is free to modify these values individually.

Scroll down window in [2], concerning the solute of interest allows the choice between 19 typical substrates. In the version of April 07, however, only the data for triolein and limonene are registered, the specific data will be displayed immediately in the subsequent edit windows. Alternatively, the scroll down menu may allow the ignoring of the substrate. This choice will lead to a copy of the specific values of the solvent into the edit window of the substrate specifications.

The user is also free to modify the molecular sum formula individually. This action will influences the calculation of the molecular diameter and viscosity.
Physicochemical parameters ($T_c$, $P_c$, $V_c$, $M$) are displayed in frame part [3]. The values are product specific and will be used for subsequent calculations of viscosity, density, diffusion coefficient. Most of these data can be found in data bases.

In frame part [4], data for molecular diameter, viscosity at norm conditions and diffusion at norm conditions can be edited. These values are used as reference for the subsequent calculation at process conditions.
- molecular diameter can either be “guessed” or cited from literature, or calculated according the formula of Brauer.
- viscosity at norm conditions can either be “guessed” or cited from literature, calculated according the formula for the hard sphere model, or using the procedure given in Reid.
- calculation of diffusion coefficient at norm pressure can be done with different options:
  a. Fullers group contribution method
  b. Wilke Chang self diffusion coefficient for gases
  c. Slattery Bird
  d. Catchpole

The buttons in frame part [5] allow to cancel/ reset the calculations, or to update resp. register the data for the upcoming calculations. By pushing the OK-button, data will be updated, the window will be closed and the user arrives in the main menu.
B. Batch

The “Batch” Form will be called from the scroll-down menu “Data Preparation” [1]. Important macroscopic information on the substrate and the natural matrix is handled.

![Batch properties form](image)

**Figure 6.4**: Batch properties form

The first action concerns a choice of the particle shape. One may distinguish between sphere, “open” cylinder, “closed” cylinder, and Ellipse. Open cylinders differ from closed cylinders by their additional active surface for mass transfer at the top and bottom plate. Choice of particle shape is done by clicking on the specific radio button in frame [2].

The form section [3] includes 2 columns: the left column consists of Edit windows, the right column contains scroll-down menus which allow to implement additional information or formula concerning the edit window which is situated on the left.

- Particle radius is essential for calculating the active surface for mass transfer as well as the path length for diffusion.
- Depending on the shape of the particle, the edit window l/r allows to calculate the height of the cylinder resp. the diameter of the broad side of a flat ellipsoid (l/r > 2!). For spheres, l/r = 2.
- Bulk porosity is an external value which should be estimated by the user (guess, Hg or N2-porosimetry).
- Pore size is an external parameter which should be estimated by the user (guess, photometry)
- Characteristic length is an important parameter which allows to estimate the mass transfer on non-spherical particles. The definition is

$$L_{\text{part}} = \frac{A}{U_s}$$

with

- $A$ : Particle surface open for mass transfer
- $U_s$ : perimeter of the “shadow” relative to fluid direction

One may obtain:

- $L_{\text{part}} := d_{\text{part}}$ for a sphere
- $L_{\text{part}} := 3.d_{\text{part}}/2$ for a cylinder being fluidised longitudinally
- $L_{\text{part}} := 3.\pi.d_{\text{part}}/8$ for a cylinder being fluidized transversally

In this simulation tool, a non-structured fixed bed has been assumed, therefore the average value of the two extreme positions (longitudinally, transversally) has been chosen.

- Specific surface is traditionally defined with the ratio of particle surface vs volume, the calculation routine is implemented

- Initial Bulk density is shall be implemented individually, it is the ratio of batch mass vs active extractor volume. A swelling of the material has been neglected.

- The parameters tortuosity and serial/parallel ($\tau$, $\phi$) may be used later-on for different options concerning the efficient diffusion coefficient. If available, tortuosity may be estimated using the method of Uquiche and Delvalle, the serial/parallel ratio inside the fixed bed matrix may be used in the estimation according chapter 4.1. $\phi$ is considered as adaption parameter, one suggestion of can be found by Schlünder ($\phi=0.2$)

- The initial concentration of the substrate in the natural matrix has a very important impact on the precision and reliability of the simulation. The discussion of this problem has been done in chapter 3.5. When defining the value in the edit window, the user should give the additional information on the source of this data (Soxhlet, Steam Distillation or maximum SFE yield). The edit window interacts with the experimental data table of this program which will be discussed later.
C. Column Data

“Column Data” is a sub form from the scroll down menu “Data Preparation” [1]

The form “column data” focuses on macroscopic information concerning column design and fixed bed structure. Depending on the geometrical values in the Edit windows [2], additional control information (Volume, Bulk mass, substrate mass) can be delivered. The values which are displayed in the sector [3] shall be verified with the “bulk porosity” and “Initial Concentration” value in the “Batch” form.

The definition of “run time”[2] will also define the final time position of the simulation.

The user may choose between the gravimetric and the non-gravimetric flow direction, which will be of use for subsequent fluid dynamic calculations (Reynolds and Grashof-Number) [4].

Side wall effects like bypass (ratio of intersections) and bypass porosity (ratio of side wall to central porosity) may be mentioned in the form section [5], they will be used in the calculation of the apparent Sherwood Number. The influence can be neglected, if desired. The overall porosity is the weighted average of the local porosities.

Figure 6.5 : Column data form
D. Process Conditions

“Process conditions” is a sub form from the scroll down menu “Data Preparation” [1]

The form “Process Conditions” will require the input of Process Pressure, Temperature and Solvent flow rate [2]. Depending on the values in the edit windows and the stocked data from the above mentioned forms, the information on reduced temperature, reduced pressure and solvent/feed ratio will be shown [3].

Solvent to feed ratio is defined as

$$S / F = \frac{n_{\text{solvent}}}{m_{\text{batch}}}$$  (6.7)

As the mass balances are structurally the same, the program offers the option of testing frontal chromatography. In this case the solvent is loaded with the compound of interest, with solvent concentration >0, whereas (in the Batch form) initial concentration of the matrix may be defined to zero.

For day to day extraction studies, the solvent concentration is zero.
6.2.3 Physical Chemistry

The forms which have been filled in the “Data Preparation” section, contain the necessary information for the subsequent calculation of the necessary dependent process parameters like density, viscosity, (effective) diffusion coefficient and axial dispersion.

The scroll down menu “Physical Chemistry” contains two options. Properties and Fluid dynamics

A. Properties

![Figure 6.6: Physicochemical Parameters at process conditions](image)

The upper section [1] of the window repeats useful and most relevant information which has been upcated from the data preparation menu.

In the medium part of the frame [2], some central parameters for the mass balance at given pressure and temperature will be defined

- density
- viscosity
- binary diffusion coefficient
- effective diffusion coefficient
- solubility

The user may edit the data manually or use the options which are proposed by the connected scroll down menus. A change in one edit window may influence the results in the following procedures, e.g. change in density influences the viscosity.
- The program provides the Benders equation for calculating the density of CO\(_2\), the density can be calculated according Benders equation. More information is available at chapter 3.2.

- Viscosity can be calculated according Jossi’s equation, which depends on the reference values at norm conditions, as well as the reduced density of the fluid. Jossi’s equation is given in chapter 3.2.

- Binary diffusion coefficient can be calculated according the equations proposed by Funazukuri (1992), Slattery-Bird (1958), Scheibel (1954), Reddy (1967) Luis Ratcliff (1968), Catchpole (1991/1994) and He (1997). If the process parameters are out of the reliability range, the values are coloured in red. Alternatively, binary diffusion coefficient can be defined individually.

- As described in chapter 4, the effective diffusion coefficient is difficult to obtain by a direct calculation procedure, and it is often suggested to select an adapted value. This program offers the option for calculating as well as for adapting to experimental values the both approaches. The value can later be modified. The numerical solutions refer to chapter 4.1, using the approaches of Bartle Currie, and Uquiche (tortuosity factor). Alternatives concern the Krischer approach, which requires a liquid and a gas phase diffusion coefficient. In this case, the edit window can be used for entering the liquid one, while the information should be chosen from the scroll down menu.

- Finally, the form allows to calculate the Schmidt Number, either from the fluid phase (binary diffusion coefficient) or the effective diffusion coefficient. This actual value is only valid for information purposes, as each simulation routine will calculate independently the required Schmidt number.

There are not much literature available for a fast estimation of solubilities. Concerning CO\(_2\) – Triglyceride (bulk oil) mixtures, we can refer to DelValle et al., alternatively empirical parameters are available for using the ChraTil equation. In most cases, the citation of a data base source (depending on pressure and temperature) will give the most reliable parameters.

The information window concerning the mean error [5] has no relevance in the moment, it is used for comparisons during the iteration procedures.

Note that there are some control procedures which verify the logical reasonability for the use of the calculation procedures. If the parameters are outside the reliability interval, the calculation result will be displayed in red, or the call routine will be ignored (e.g. the attempt to use Benders equation in case of Propane as solvent).
**B. Fluid dynamics**

Diffusion, fluid density and viscosity are essential for the estimating of fluid dynamics. Based on the data obtained in the form dealing with physico-chemical parameters, it is now possible to calculate and visualise the Reynolds and Peclet numbers in the fixed bed. These figures are shown in the upper part of the fluid dynamics form.

Section [1] concludes important data relevant for the fluid dynamics, which have been updated from the previous forms:

- Schmidt number refers to the fluid phase of the fixed bed, i.e. the binary diffusion coefficient
- Velocity of the fluid phase can be calculated from mass flow, porosity and density (from the properties form)
- Grashof number includes the free and forced convection during the calculation of the fluid dynamics and its definition via the Reynolds number. Schlünder has proposed to distinguish between the particle and fixed bed Reynolds number.
- Bypass parameters are calculated according the equation 4.25 in chapter 4.6.3, it is an index for the bypass flow rate.

![Fluid and Mass Transfer: calculated / literature values](image)

*Figure 6.8: Fluid Properties at process conditions*
In section [2] axial dispersion parameters are defined

- Different options are available to calculate the axial dispersion, we may refer to Funakuzuri, Butt, Catchpole, Yu and Tan. In the range of flow velocities below 2 – 3 mm/s, the axial dispersion values reach 10–5 m²/s.
- In parallel, dispersion-dependent Sherwood number for a particle and for the fixed bed can be calculated. The options which are discussed in this work refer to Schlünder as well as Tan Liou, Catchpole, Funakuzuri, Yu.
- For defining the equation system, the values for axial dispersion can be used for calculating the number of the number of theoretical equilibrium plates. This value will be needed from the integration tool. Process responses become similar at \( N\text{Th} > 20 \) (plug flow behaviour), however, calculation time increases with \( N\text{Th} \).

The information window [3] contains useful data for the subsequent estimation of apparent parameters: Bodenstein and axial dispersion Peclet number, as well as the Number of Transfer units, when the system is considered as SSP, according chapter 4.6.2.

In the frame section [4], mass transfer constant \( \kappa \) can be consequently calculated from the Sherwood number, whereas the user may choose between the values for particle or fixed bed.

Biot number defines the slope of the concentration profile from the inner particle to the fluid phase. It can be calculated when the different mass transfer coefficients (inner particle and fluid phase) are given. A first guess can be started when binary and effective diffusion coefficient are known. Brunner (1994) has proposed a alternative version for calculating the Biot number, but it is only valid for the desorption model.

Biot number may change during the extraction and are consequently permanently actualised during the simulation progress. The value of this edit window has no significance to subsequent calculation.
6.2.4 Experimental and apparent values

The aforementioned forms conclude all data which can be calculated without any experimental extraction results. The calculations show trends for estimating the most relevant process parameters like density, viscosity, diffusion coefficient and mass transfer. Information is still missing on the desorption / resp. shrinking core behaviour, and it is a matter of fact that the calculated diffusion coefficients require some experimental verification.

The following form will introduce the missing link between theoretical estimation and experimental confirmation.

Experimental Data can be introduced into the table, which appears directly when the scroll down menu “Exper_Apparent”[1] is activated.

![Figure 6.9: Experimental data table](image)

- mass flow, fluid velocity, batch mass and characteristic length
- the saturation concentration according the results in the properties form
- recent and updated effective diffusion coefficient
- zero retention time (mean residence time) of the fluid in the extractor.
- Normed Fourier number $\Theta_e$, which is defined by Goto (equation 5.8), and may only be of use in shrinking core models
The program allows the treatment of 10 experimental points (Frame [4] and [6]). The user
disposes on several options for defining the co-ordinates of the experimental data. This will
allow a convenient access to a large variety of literature results. The choice can be done by
executing the specific radio-buttons,

x- Axis [3] :
- time (min)
- mass of solvent (g)
- mass of solvent relative to mass of batch input
- time relative to zero retention time
- dimensionless time (Fourier number), relative to recent effective Diffusion
  coefficient

y- axis [5]:
- yield in the time interval from \( t_i - t_{i-1} \) (mg)
- solute concentration in solvent in the time interval from \( t_i - t_{i-1} \) (g/kg)
- accumulated yield relative to batch input (%) 
- accumulated yield (mg)
- solute concentration in the solvent in the time interval from \( t_i - t_{i-1} \), relative to
  saturation concentration (solubility limit) ; condition is \( C / C_{sat} < 100 \% \)

It should be kept in mind that the format of the edit window matrix (scientific, digit
numbers) must be respected, otherwise an error message occurs.

When pushing the “Calculate” button [7], the program will re-calculate and display the data
of the other co-ordinates by simple mass balances. After this procedure, the button for
displaying the experimental points diagram [8] is accessible for use. Alternatively, the form
may be closed and the user arrives in the main menu.
The sub-form “Diagram” provides useful tools for estimating the efficient diffusion coefficient more precisely, referring to the constant extraction rate.

Figure 6.10: Experimental data diagram and tools for the calculation of mass transfer

Frame [1] displays the experimental results, different co-ordinate definitions may be selected. The total extraction yield curve may be obtained when the radio buttons combine “time (min)” on the x-axis with the “accumulated yield (mg)” on the y-axis.

The x-axis may display the scale of a normalized Fourier number Θ, that is the actual Fourier number in ratio to Θₑ:

The y-axis of the diagram can be visualised in decimal or logarithmic scale, using of the radio button on the top of the window

Frame [2] concludes the tools for calculating the apparent solubility. According to chapter 4.2, the apparent solubility may be calculated from the constant extraction rate section of the total extraction yield curve. The information on the time for the constant extraction rate and the Mass during the constant extraction must be given individually. The scroll down menu in frame [2] allows to distinguish between different methods.
  - entering the two edit windows (Time and Mass CER) individually
  - calculating the mass by interpolating at a given time
  - using the mouse click by indexing a co-ordinate in the diagram of the total extraction yield curve.
The information windows in frame [2] will consequently calculate the relative mass of the constant extraction rate in ratio to the total substrate (definition in the batch form), as well as the apparent solubility. The value of the apparent solubility appears in red when it is bigger then the thermodynamic solubility.

Frame [3] concludes the calculation routines for the estimation of the effective diffusion coefficient. The scroll down menu proposes different options:

- to use the effective diffusion coefficient from the calculation form of the physicochemical properties
- to iterate the wet diffusion coefficient according the simple single plate model for spheres for the whole extraction yield curve, using Krischers approach of a dynamic concentration change inporous network
- to calculate the wet phase diffusion coefficient by focussing on the constant extraction rate
- to iterate \( D_{\text{wet}} \) resp. solid phase diffusion according Schlünder by focussing on the constant extraction rate for low Peclet numbers
- to iterate \( D_{\text{wet}} \) according Schlünder by focussing on the constant extraction rate for increase Peclet numbers, that is by taking into account the axial dispersion
- to iterate \( D_{\text{wet}} \) according Schlünder by focussing on the constant extraction rate for increased Peclet numbers and by taking into account bypass effects.

The iteration is done by applying the method of smallest mean error squares between simulation and experimental result, and using the Newton-Raphson method. Due to the existence of local extrema, the actual program may not warrant the optimum value. However, an experimentally confirmed deduction of the effective diffusion coefficient is made feasible.

The result and the apparent Schmidt number are shown in frame [3]. Pressing the Plot Button will design the simulated extraction yield for a particle model in the diagram of frame [1], according to the above mentioned procedures (Desorption and Shrinking core effects are not taken into account).

In Frame [4], additional information for the apparent Sherwood number and the apparent mass transfer rate is displayed. It may be edited from the user for individual studies on the sensitivity.

The OK-Button will close the diagram frame, the values will be updated and the experimental value form will re-appear.
6.2.5 Simulation Tool

The program version April 07 implicates 3 simulation options:
- Sovova Model
- Shrinking Core Model
- Desorption -Diffusion – Dispersion model

Other routines are in preparation

A: Sovova Model

Under condition that saturation concentration and constant extraction rate are defined, the Sovova Model does not require any additional parameters for modelling. It should be noted that values on diffusivity and viscosity are not required as input parameters in this model, however, they can be deduced from the output as a function of the constant extraction rate section.

Frame [1] includes the updated values resulting from the experimental total extraction yield:
- time of constant extraction rate
- mass of constant extraction rate
- relative yield from constant extraction rate

Frame [2] displays the calculated saturation concentration, which has been defined in the properties form.

Frame [3] will allow to optimise the time resp. mass of constant extraction rate so that the sum of error squares between simulation and experimental curve becomes minimal. However, iteration and calculations are yet very often unstable.

![Figure 6.11: Sovova model, relevant data](image)

Pushing the “Calculate” button will start the analytical simulation function, and a new diagram window will be opened.
The diagram frame shows simulated and experimental total extraction yield curve, and displays the calculated data concerning the mass transfer:

![Sovova Model, Simulation output](image)

**Figure 6.12** :Sovova Model, Simulation output

The relevant data output [1] concerns
- the product of mass transfer rate and specific surface concerning solid and fluid phase \((\kappa a)\)
- the mass transfer rate concerning solid and fluid phase \((\kappa)\), as well as the overall mass transfer rate
- the calculated diffusion coefficients for solid and fluid phase \((\delta)\), which may differ from the estimated one.

A reliability check can be performed easily when comparing the two values, commonly the transfer in the fluid phase is faster than in the solid phase.

The simulation protocol can be saved to an Excel file by pushing the “Save Report” Button [3]. The user shall take care on the extension “.xls” in the file handling form.

When pushing the “close” button [2], the user re-enters the main menu.

If a system error occurs, most probably the input parameters (Initial Concentration of the bulk material, tCER and MCER, as well as saturation concentration) should be re-validated.
B Shrinking Core Model

Program Version of April 07 is limited on spherical parameters, modifications according Stüber and al are in preparation.

The Goto Shrinking Core Model uses two parameters which are not directly accessible, that is the effective diffusion coefficient and a (constant) Biot number.

As a system of differential equations must be solved, the program requires additional support parameters for the solver.

![Figure 6.13: Goto Model: Relevant Simulation Data](image)

Frame [1] displays the integrator support values in Edit windows.
- For stable integrations, precision should not exceed the value of $10^{-5}$.
- The number of collocation points should be at least twice as the run time in minutes. In this case it is assured that each experimental time position is placed inside the Pivot interval of the Newton-Raphson error estimation..
- The initial time switch step should be not greater then $10^{-5}$.

However, the more precise the calculation, the longer is the simulation run time.
Frame [1] includes also a series of check boxes which allow additional options for more precise simulation. The user may choose:

- the re-calculation of the fluid density in function of its actual substrate loading. This means that at each time step and at each local position, the influence of substrate density will be taken into account for estimating the fluid density. One may consider some relevant effects especially in the case of bulk oil extractions, when the solvent may be loaded with about 3% of substrate.
- the re-calculation of the fluid viscosity in function of its actual substrate loading and actual density. This means that at each time step and at each local position, the influence of substrate viscosity will be taken into account for estimating the fluid viscosity. One may consider some relevant effects especially in the case of bulk oil extractions, when the solvent may be loaded with about 3% of substrate.
- the re-calculation of the binary diffusivity in function of its actual (local) substrate density and viscosity.
- The calculation of the effective diffusion coefficient by means of the Krischer Model. In this case, the binary diffusion coefficient and the solid phase diffusion coefficient will be combined in function of the actual substrate loading, according to chapter 4.6.3.

Frame [2] updates the recent parameters, mainly for information purposes:

- Pressure, Temperature and (initial) density of the pure solvent
- (initial) Reynolds Number of the pure solvent
- Axial Dispersion and updated effective Diffusion coefficient
- Schmidt Number relative to the effective diffusion coefficient
- Dimensionless numbers a and b concerning concentration and mass transfer capacity of the shrinking core model (see equation)
- Peclet Number relative to the particle diameter
- Sum of error squares

Provided that saturation concentration and initial concentration are precisely defined, Biot number remains the only adapting parameter.

Frame [3] includes the menu for the choice of the Biot Number, and its influence on the overall mass transfer as well as the apparent Sherwood number:

- optionally, Biot can be calculated from the overall mass transfer value resulting from the experimental curve
- alternatively, Biot number can be chosen individually, at a given effective diffusion coefficient. Consequently kappa and Sherwood number will change.
- The option for automatic iterating of the optimum Biot number is in preparation (April 2007)
Pushing the “Calculate” Button will open the diagram form which shows the experimental and simulation results.

The diagram displays two versions of the y-Axis:
- on the left side, the solute concentration in the solvent, relative to the saturation concentration is shown. Realistic experimental and simulation curves shall not exceed the limit of 100 %. Concentration function and experimental values are designed in green.
- On the right side, the total extraction yield relative to the batch raw material input is shown. Yield function and experimental values are designed in blue.

Frame part [2] collects the data of this simulation. Biot number was the only adapting parameter.

When large discrepancies between simulation and experimental results occur, the reason is placed in most cases in an imprecise estimation of the initial substrate concentration of the bulk as well as the saturation concentration.

The simulation protocol can be saved to an Excel file by pushing the “Save Report” Button. The user shall take care on the extension “.xls” in the file handling form.

When pushing the “close” button, the user re-enters the main menu.
C. Diffusion – Desorption – Dispersion Model

The Diffusion – Desorption – Dispersion Model, as proposed by Brunner, uses two (resp. three) parameters, which are not explicitly previsible.

- the effective solid phase diffusion coefficient, resp. the overall mass transfer coefficient
- the Biot number
- the desorption equilibrium

Methods how to estimate the overall mass transfer coefficient are given in this work. Fluid phase mass transfer can be estimated via the binary diffusion coefficient. For estimating the Biot Number, Brunner proposes a combination with the desorption resp. distribution coefficient.

\[
K = k_{1} \cdot \hat{c}^{-1/2}
\]

\[
Bi = \frac{\kappa_{\text{fluid}} \cdot R}{\delta_{\text{solid}}} \cdot K
\]

The form structure of the DDD model is equivalent to the Goto shrinking core model.

![Figure 6.13: DDD Model: Relevant Simulation Data](image-url)
Frame [1] displays the integrator support values in Edit windows.
- For stable integrations, precision should not exceed the value of $10^{-5}$.
- The number of collocation points should be at least as great as the run time in minutes.
- The initial time switch step should be not greater then $10^{-5}$.

However, the more precise the calculation, the longer is the simulation run time.

Frame [1] includes also a series of check boxes which allow additional options for more precise simulation. The user may chose
- the re-calculation of the fluid density in function of its actual substrate loading. This means that at each time step and at each local position, the influence of substrate densities will be taken into account for estimating the fluid density. One may consider some relevant effects especially in the case of bulk oil extractions, when the solvent may be loaded with about 3% of substrate.
- the re-calculation of the fluid viscosity in function of its actual substrate loading and actual density. This means that at each time step and at each local position, the influence of substrate viscosity will be taken into account for estimating the fluid viscosity. One may consider some relevant effects especially in the case of bulk oil extractions, when the solvent may be loaded with about 3% of substrate.
- the re-calculation of the binary diffusivity in function of its actual substrate density and viscosity.
- The calculation of the effective diffusion coefficient by means of the Krischer Model. In this case, the binary diffusion coefficient and the solid phase diffusion coefficient will be combined in function of the actual substrate loading, according to chapter 4.2

Frame [2] updates the recent parameters, mainly for information purposes
- Pressure, Temperature and (initial) density of the pure solvent
- (initial) Reynolds Number of the pure solvent
- axial Dispersion and updated effective Diffusion coefficient
- Schmidt Number relative to the effective diffusion coefficient
- Apparent mass transfer number
- Peclet Number relative to the particle diameter
- Sum of error squares

Provided that saturation concentration and initial concentration are precisely defined, Biot number remains the only adapting parameter.

Frame [3] includes the menu for the choice of the Freundlich parameters which allow to estimate the desorption equilibrium $K$.
The scroll down menu allows to iterate $k_1$ at a constant $k_2$ value, as well as $k_2$ at given $k_1$. Iteration will be executed according the Newton-Raphson method, whereas the smallest error square indexes optimum choice of the desorption constant.

Pushing the calculate button will iterate/calculate the simulation program and display the extraction yield curves:
The diagram displays two versions of the y-Axis:
- on the left side, the solute concentration in the solvent, relative to the saturation concentration is shown. Realistic experimental and simulation curves shall not exceed the limit of 100%. Concentration function and experimental values are designed in green.
- On the right side, the total extraction yield relative to the batch raw material input is shown. Yield function and experimental values are designed in blue.

Frame part [2] collects the data of this simulation. Desorption constants k1 and k2 are the only adapting parameter. The effective solid phase diffusion coefficient is one important calculation output from the VTII model.

When large discrepancies between simulation and experimental results occur, the reason is placed in most cases in an imprecise estimation of the initial substrate concentration of the bulk as well as the saturation concentration.

The simulation protocol can be saved to an Excel file by pushing the “Save Report” Button. The user shall take care on the extension “.xls” in the file handling form.

When pushing the “close” button, the user re-enters the main menu.
6.3 Simulation Protocols

When pushing the “save result” button, a protocol file in Excel format will be created. It includes all experimental and simulated parameters. When importing the file to the Excel program, it is advised to apply the text converting routine (step 3 of 3, [0]), and selecting the push button for additional options[1]: The decimal digit separation symbol shall be a point, whereas no definition is required for the separation of the dimension $10^3$. That means, that the upper scroll down menu[2] shall indicate the point, whereas the bottom menu[3] shall indicate a void field.

Figure 6.18: Simulation Protocol in Excel Format