A Fast Method for the Prediction of Breakthrough Curves of Non-Isothermal Fixed-Bed Reactors

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SUMMARY

A model and a computer program have been developed for the prediction of breakthrough curves of a non-isothermal adsorption column, packed with porous spherical particles. At time zero, a step change in the concentration of an adsorbable component is introduced to the flowing stream. Together with this concentration step, the temperature of the flowing stream may be changed.

The adsorption column is subjected to axial dispersion, external film diffusion resistance, pore diffusion resistance, heat effects of the adsorption process, axial heat transfer resistance of the solid and the fluid phase, external film heat transfer resistance and heat transfer from the fluid and the solid phase to the wall. Radial gradients, the pressure drop across the bed, mass accumulation in the pores and the heat capacity of the fluid in the pores are neglected. Other assumptions are: plug flow takes place in the bed; heat capacities, densities and the adsorption heat are constant with respect to concentrations, temperatures and time; and the wall temperature is uniform and constant. At the solid surface, the fluid phase and solid phase are assumed to be in equilibrium. This equilibrium must be represented by an isotherm that is linear with respect to concentration and temperature, because for the method of solution, this isotherm must be Laplace transformed.

The model equations are solved by Laplace transformation, both with respect to time and place. The inverse Laplace transform with respect to place is calculated analytically by complex integration. The inverse Laplace transform with respect to time is calculated numerically by applying the Fast Fourier Transform. As a result, the computer program calculates concentration and temperature breakthrough curves in a few minutes on a Personal Computer with a 8086 processor and a 8087 mathematical coprocessor.

The model describes quantitative the existence of different breakthrough regimes and temperature plateaus. The effects of variations of the process parameters, such as diffusion coefficients and heat transfer resistances are described qualitative.

In order to make the program useful for a more general set of fixed-bed processes, future developments should be directed towards a more general adsorption isotherm and the radial components of the model equations. Especially the possibility of non-linear isotherms would make the program very powerful.
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CHAPTER 1

INTRODUCTION

The purpose of this study was to develop a model and a computer program for the description of non-isothermal fixed-bed processes. The original reason for this, were laboratory-scale experiments of the regeneration step of a process that removes H₂S from gas streams (van der Wal, 1987).

This proved to be a process with a high degree of complexity; H₂S is removed in a fixed-bed reactor, filled with porous silica particles on which iron oxide is deposited. Reaction products are water and iron sulfide on silica. During the regeneration step, iron sulfide is reoxidized to iron oxide with the aid of oxygen. Also SO₂ and elemental sulfur are formed. The production of elemental sulfur is preferred, but the process conditions for the formation of sulfur are very strict. At temperatures higher than 300°C, much SO₂ is formed, and at temperatures lower than 250°C, the pores of the sorbent are plugged by condensed sulfur. The effects of non-ideal plug flow, caused by a less dense packing at the wall are expected to be important.

The development of a model for the process above had been a step-wise process, starting with an isothermal reactor without radial gradients. Chen and Hsu (1987) describe how the model equations for an isothermal adsorption process can be solved by applying the Fast Fourier Transform (FFT) method for the solution of differential equations. This appeared to be a very fast method for the prediction of breakthrough curves. Therefore, it had been decided to try to apply this FFT method for the description of a non-isothermal adsorption process. The model for the isothermal process had been extended with heat effects. First, one temperature for both fluid and solid phase had been introduced. Later on, two separate temperatures for fluid and solid phase had been assumed. The radial gradients are not yet included in the program.

This report is divided into the following sections:

In chapter 2, a description of fixed-bed reactors, and some theory about breakthrough curves and adsorption isotherms is given.

After a description of the mass and heat transfer mechanisms included in the model, the model equations are developed in chapter 3.

The mathematical methods used for the solution of the model equations are explained in chapter 4.

Chapter 5 describes how the model equations can be solved.
In chapter 6, the computer program is described. Guidelines for the input are given and numerical problems are discussed.

Results and discussion are given in chapter 7 and 8.

In appendices A, B and C, the procedures of the computer program are listed. In appendix D, numerical values of different breakthrough curves are given.

Although radial gradients are not included in the program, the model equations for a reactor with radial gradients of concentrations and temperatures are given in appendix E.
Figure 2.1 Schematic representation of a fixed-bed reactor

Figure 2.2 Variables that are functions of time and place
CHAPTER 2

ADSORPTION AND REACTION PROCESSES IN FIXED-BED REACTORS

2.1 Fixed-Bed Reactors

In this thesis non-stationary fixed-bed processes are considered, such as adsorption processes and gas-solid reactions. Most often, they physically consist of a tube (or tube bundle), which is packed with solid particles and on which a reactant can be deposited (figure 2.1). The reactants enter at one end of the tube, and the reaction products are withdrawn from the other end.

At a fixed concentration of reacting components and temperature, the reaction- or adsorption rate is directly proportional to the solid surface area. Therefore, highly porous particles are preferred.

A variety of gradients in reactants concentrations and temperatures exist within a fixed-bed reactor. Since reaction(s) proceed along the tube length, there are obvious gradients in concentrations, and fluid and solid temperatures in the axial direction. Because of heat transfer at the tube wall between the reacting mixture and the, often cooled, wall, radial gradients in temperatures and concentrations exist. At any location within the tube, there are concentration and temperature gradients between the fluid and solid phases. Finally, there are reactant concentration (but negligible temperature) gradients within each of the individual solid particles. Because the process is non-stationary, all these gradients are varying as a function of time.

There are five concentrations and temperatures varying with time and position in the reactor: the reactant concentration in the fluid \( (c_r) \), the concentration of the fluid in the pores \( (c_s) \), the adsorbed concentration \( (q) \) and the temperatures of the fluid \( (T_r) \) and solid \( (T_s) \), (figure 2.2).

2.2 Breakthrough Curves

For the non-stationary processes considered, the reacting components penetrating into the bed will form an adsorption zone that moves through the reactor and that will finally leave the reactor. The mechanisms taking place can be described by the shape of the front at the end of the reactor. A plot of the concentration or the temperature of the effluent versus time is called a breakthrough curve.
Figure 2.3 Example of an isotherm

Figure 2.4 Distance-time plot showing fluid concentration curves for unfavorable equilibrium (Perry, 1985)

Figure 2.5 Distance-time plot showing fluid concentration curves for favorable equilibrium (Perry, 1985)
For reacting systems with a specified maximum allowable reactants concentration in the effluent, steep breakthrough curves are preferred. When a concentration step is introduced in any imaginary fixed-bed reactor without dispersion effects and mass transfer resistances, the breakthrough curve will exactly be that step. Unfortunately, ideal reactors without dispersion effects and mass transfer resistances do not exist. In a real fixed-bed reactor dispersion and mass transfer resistances, such as pore diffusion, have a spreading effect on the breakthrough curve. Therefore the ideal step breakthrough curve will change to an S-shaped curve.

Analogous to the concentration breakthrough curve, the temperature breakthrough curve is spread by the different heat transfer mechanisms, such as heat transfer through the film around the solid phase. Because a specification for the effluent is in general only given for the concentration of the reactant, the shape of the temperature breakthrough curve is less important.

2.3 Adsorption Isotherms

An important factor in adsorption processes is the equilibrium between the fluid phase in the pores and the adsorbed phase at the surface. An adsorption isotherm describes for a specified temperature, how the adsorbed concentration \( q \) is varying with the fluid concentration \( c_a \). An example is given in figure 2.3. Commonly used isotherms are those of Langmuir and Freundlich (Perry, 1985). Two major types of adsorption isotherms can be distinguished, unfavorable isotherms and favorable isotherms.

An unfavorable equilibrium is characterized by a concave-upward plot of \( q \) versus \( c_a \). In this case the moving front is continuously broadened. The width is proportional to the distance from the bed entrance and therefore this phenomenon is called Proportional Pattern behaviour (figure 2.4).

A favorable equilibrium is characterized by a convex-upward isotherm. When a step change of concentration is introduced, the initially abrupt zone front will be broadened to a certain extent. In the case of a broader, smaller-slope zone, it will be sharpened until the same constant shape is reached. This phenomenon is called Constant Pattern behaviour (figure 2.5).

Whether a Proportional Pattern or Constant Pattern behaviour will be established can be deduced theoretically from the shape of the isotherm. When diffusion terms are neglected, the mass balance for both the fluid and solid phase in a slice of the reactor can be written as

\[
\frac{\partial c_f}{\partial t} + \frac{\partial c_f}{\partial z} + \frac{1}{\varepsilon} \frac{\partial q}{\partial t} z = 0
\]  

(2.1)
From the equilibrium in the pores follows, when pore and film
diffusion are neglected:

\[
\frac{\partial q}{\partial t} = \frac{\partial c_f}{\partial t} \cdot \frac{dq^*}{dc_a} \tag{2.2}
\]

where \(dq^*/dc_a\) is the slope of the isotherm for a specified \(c_a\).

Substitution of equation (2.2) in (2.1) gives:

\[
v \left( \frac{\partial c_f}{\partial z} \right)_t + \left( \frac{\partial c_f}{\partial t} \right)_z \cdot \left[ 1 + \frac{1-\epsilon}{\epsilon} \frac{dq^*}{dc_a} \right] = 0 \tag{2.3}
\]

From (2.3) follows:

\[
\frac{dz}{dt}_c = \frac{v}{1 + \frac{1-\epsilon}{\epsilon} \frac{dq^*}{dc_a}} \tag{2.4}
\]

In this equation \((dz/dt)_c\) is the propagation velocity of fluid
with a concentration \(c\).

For a favorable isotherm, \(dq^*/dc\) is higher for low concen­
trations than for high concentrations. This would mean that the
propagation velocity of high concentrations is higher than the
velocity of low concentrations. Physically however, this is
impossible. In reality all velocities will become the same, and
the tendency of high concentrations to go faster than low
concentrations results in a self-sharpening front. An abrupt
front however, will not be formed because an equilibrium will
be developed with the mass transfer resistances which have a
spreading effect on the front. When the self-sharpening front
has reached equilibrium, it will move unchanged through the
rest of the bed.

For an unfavorable isotherm, the opposite counts. Low concen­
trations have a higher velocity than higher concentrations,
leading to continuous spreading.

2.4 Relative Velocities of Concentration and Temperature
Fronts

In a non-isothermal fixed-bed reactor, the fluid acts as a
carrier for both the reacting components and the thermal energy
released in the adsorption process. The resulting concentration
and temperature waves move through the bed at velocities which
Figure 2.6 Pure thermal wave breakthrough curves

Figure 2.7 Combined wave breakthrough curves
are determined by the thermal, adsorptive and transport characteristics of the reactor, as well as the fluid flow rate. Depending on the relative magnitude of these parameters, different shapes and combinations of concentration and temperature waves are possible. There are two major cases (Fan and Basmadjian 1970):

1 - Pure thermal wave
   In this case the temperature front moves through the bed ahead of the adsorbate front. This is illustrated in figure 2.6

2 - Combined wave
   In this case the concentration breakthrough is together with the temperature breakthrough, followed by a plateau of constant concentration and temperature (figure 2.7). After some time, the concentration and temperature will reach their stationary values.

First an equation will be deduced for the magnitude of the plateau temperature. Then conditions are given for the existence of the two types of fronts.

2.4.1 Magnitude of the temperature step of the front

The magnitude of the temperature step of the front can be calculated from the mass and heat balances for the slice of the reactor in which the front is moving (figure 2.8).

When the accumulation of mass in the fluid is neglected, the mass balance is given by:

\[ \varepsilon v n R^2 c_{f1} = \varepsilon v n R^2 c_{f2} - (q_2 - q_1)(1 - \varepsilon) \left[ \frac{\partial z}{\partial t} \right]_{\text{front}} \]  

(2.5)

From (2.5) follows:

\[ \frac{\varepsilon v}{(1 - \varepsilon) \beta} = \frac{q_2 - q_1}{c_{f2} - c_{f1}} \]  

(2.6)

with \( \beta = \left[ \frac{\partial z}{\partial t} \right]_{\text{front}} \)

The heat balance is given by:

\[ \varepsilon v n R^2 C_{pr} \rho_f T_1 = \varepsilon v n R^2 C_{pr} \rho_f T_2 - (q_2 - q_1) \Delta H \beta n R^2 (1 - \varepsilon) - C_{p_b} \rho_b (1 - \varepsilon) \beta n R^2 (T_2 - T_1) \]  

(2.7)
Figure 2.8 Slice of the reactor with a concentration front
With substitution of equation (2.6) this can be reduced to:

\[
T_1 - T_2 = \frac{-\Delta H}{C_p f \cdot \rho_f - C_p s \cdot \rho_s \over c_{f1} - c_{f1}} - \frac{q_2 - q_1}{q_2 - q_1} 
\]  

(2.8)

In the same way can be deduced:

\[
T_2 - T_3 = \frac{-\Delta H}{C_p f \cdot \rho_f - C_p s \cdot \rho_s \over c_{f2} - c_{f2}} - \frac{q_3 - q_2}{q_3 - q_2} 
\]  

(2.9)

2.4.2 Velocities of concentration and temperature waves

The velocity of the concentration front of an isothermal process follows from equation (2.5):

\[
\frac{\delta z}{\delta t} = \frac{c_{f2} - c_{f1}}{q_2 - q_1} \cdot \frac{v \cdot \epsilon}{1 - \epsilon} = \beta_{iso th} 
\]  

(2.10)

Because the adsorption capacity is lower at higher temperatures, any temperature rise during the adsorption process will have the effect of enhancing the velocity of the concentration front, so that \( \beta > \beta_{iso th} \).

The velocity of a temperature wave in the reactor can be deduced from the heat balance for the reactor. If the heat resistances are neglected, and thus, solid and fluid have the same temperature, the heat balance for a slice of the reactor is reduced to:

\[
\frac{\delta T}{\delta z} + \frac{(1-\epsilon) \cdot \rho_s \cdot C_p s \cdot \delta T}{\delta t} = 0 
\]  

(2.11)

where the accumulation of heat in the fluid phase is neglected. From this follows:

\[
\frac{\delta z}{\delta t} = \frac{\rho_f \cdot C_p f \cdot v \cdot \epsilon}{\rho_s \cdot C_p s \cdot (1-\epsilon)} = \alpha 
\]  

(2.12)

where \( \alpha \) is the velocity of propagation of a particular temperature level in the temperature wave, which is seen to be independent of \( T \).
Comparison of equations (2.10) and (2.12) shows that the concentration front velocity for an isothermal process, and thus the concentration front velocity for a non-isothermal process, is greater than the velocity of the temperature front when:

\[
\frac{\rho_s \cdot C_{ps}}{\rho_f \cdot C_{pr}} > \frac{q_2 - q_1}{C_{f2} - C_{f1}}
\]  (2.13)

In this case, it is impossible for a pure thermal wave to pull ahead of the adsorption zone, since the combined wave will propagate faster than a pure thermal wave would do. Equation (2.13) is therefore a sufficient condition for the existence of a combined wave front. However, the inverse relation

\[
\frac{\rho_s \cdot C_{ps}}{\rho_f \cdot C_{pr}} < \frac{q_2 - q_1}{C_{f2} - C_{f1}}
\]  (2.14)

represents only a necessary condition for a pure thermal wave. For systems obeying relation (2.14), Pan and Basmadjian (1970) give the condition

\[
\frac{\rho_s \cdot C_{ps}}{\rho_f \cdot C_{pr}} < \frac{q^*(T_{2\text{max}}, c_{f1})}{C_{f1}}
\]  (2.15)

where \(T_{2\text{max}}\) is the maximum temperature that can be reached at the plateau. Equations (2.14) and (2.15) are sufficient conditions for the existence of a pure thermal wave. The maximum temperature can be shown to occur at \(T_2 = 0\) and is easily deduced from equation (2.9):

\[
T_{2\text{max}} = T_3 + \frac{-\Delta H}{C_{pr} \cdot \rho_r - C_{ps} \cdot \rho_s}
\]  (2.16)

\(q^*(T_{2\text{max}}, c_{f1})\) is the adsorbed concentration in equilibrium with \(c_{f1}\) at \(T_{2\text{max}}\).

In systems obeying equation (2.14) but not equation (2.15), formation of either a combined front or a pure thermal wave is possible in principle (Pan and Basmadjian, 1970).

Mass transfer mechanisms that are included in the model
3.1 Purpose of the Model

A model has been developed for a non-isothermal adsorption process in a fixed-bed reactor with porous solid particles. In paragraph 3.7 will be described under what conditions this model can be applied for gas-solid reactions in fixed-beds.

If the process parameters of a system, such as diffusion coefficients and heat transfer coefficients, are known, the model can be used for the prediction of breakthrough curves. If the parameters are assumed to be correct, deviations between the predicted curves and correctly measured curves then indicate that the model does not give a good description of the process.

The model can also be used for the determination of process parameters. In this case, measured breakthrough curves must be fitted by the model. The parameters used for the best fit will be an estimation of the real parameters. It must be certain that the model can describe the system correctly. Care must be taken for models with many parameters. In that case many breakthrough curves must be fitted to get reliable parameter estimations, because a single curve can usually be fitted by a widely varying set of parameters.

3.2 Mass Transfer Mechanisms

In paragraph 2.2 has been explained that the mass and heat transfer resistances are responsible for the broadening of the breakthrough curves. These effects will be discussed in detail in this and the next paragraph.

The following mass transfer mechanisms have been taken into account (figure 3.1):

1 - Fluid phase axial diffusion and dispersion
2 - Mass transfer resistance of the film around the solid phase
3 - Pore diffusion in the fluid phase

Transport- and diffusion coefficients are constant with respect to time, concentrations and temperatures.

ad.1 Dispersion is caused by the phenomenon that the fluid has to flow around the particles. Even with very low flow velocities there will be a break up and mixing of parts of the fluid. With higher flow velocities
Figure 3.2  Heat transfer mechanisms that are included in the model
this effect will be greater because of turbulency. Generally, the contribution of the diffusion will be small compared with these effects. All these effects are included in the axial dispersion coefficient $D_a$. In a cross section of the reactor the mass flow as a result of dispersion is

$$\frac{dc_f}{dz} = D_a \cdot nR^2 \cdot \cdot$$

Because the flowrate at the surface of the solid particles is zero, a thin stagnant film will surround the pellets. In general, the mass transfer resistance of this film will be small. However, Chen and Hsu (1987) take this effect into account. For comparison with their results the film resistance, given by the mass transfer coefficient $k_f$, is included in the model. The mass transfer through the film around a spherical particle is

$$k_f \cdot 4\pi R_p^2 \cdot (c_f - c_a) \bigg|_{r_p=R_p}$$

After passing the film, the reactant has to diffuse into the pore to the free adsorbent surface. The mass transfer through a sphere in the particle at a distance $r_p$ from the center of the particle is

$$\frac{dc_a}{dr_p} = D_p \cdot 4\pi r_p^2 \cdot$$

in which $D_p$ is the pore diffusion coefficient.

### 3.3 Heat Transfer Mechanisms

The following heat transfer mechanisms have been considered (figure 3.2):

1. Fluid phase axial heat conduction and dispersion
2. Solid phase axial heat conduction
3. Heat transfer resistance of the film around the solid phase
4. Heat transfer from the fluid phase to the wall
5. Heat transfer from the solid phase to the wall

Transport coefficients are constant with respect to time, concentrations and temperatures.

Fluid dispersion will also have a spreading effect on the temperature breakthrough curve. Analogous to the mass dispersion coefficient, the heat conduction coefficient $\lambda_f$, takes into account the effects of heat conduction and dispersion. In a cross section
of the reactor, the heat transport as a result of conduction and dispersion in the fluid phase is given by

\[
\frac{dT_f}{dz} - \lambda_f . nR^2 . \varepsilon \frac{dT_f}{dz}
\]

ad.2 The solid phase axial heat transfer conduction is given by the heat transfer coefficient \( \lambda_s \). In a cross section of the reactor the heat conduction in the solid phase is

\[
\frac{dT_s}{dz} - \lambda_s . nR^2 . (1-\varepsilon) \frac{dT_s}{dz}
\]

ad.3 In contrast to the mass transfer resistance, the heat transfer resistance of the film around the solid phase can generally not be neglected. The heat transfer through the film around a spherical particle is

\[
h_f . 4nR_p^2 . (T_s \bigg|_{r_p=R_p} - T_s)
\]

with \( h_f \) the heat transfer coefficient

ad.4/5 From both the fluid and the solid phase heat is transported to the wall. These effects are given by the heat transfer coefficients \( h_{wf} \) and \( h_{ws} \), respectively. The heat transfer from the fluid to the wall in a slice of the reactor with length \( \Delta z \) is

\[
h_{wf} . (T_f - T_{wa1}) . 2nR\Delta z . \varepsilon
\]

and from the solid to the wall

\[
h_{ws} . (T_s - T_{wa1}) . 2nR\Delta z . (1-\varepsilon)
\]

3.4 Heat Production

In adsorption processes, generally heat effects will take place. The adsorption heat \( (-\Delta H) \) is the quantity of heat released when one mole reactant is adsorbed. The heat effect in a slice of the reactor with volume \( \Delta V \) is then given by

\[
\frac{dq}{dt} = (-\Delta H) . (1-\varepsilon) . \Delta V
\]
3.5 Simplifying Considerations

Not all effects that can take place in a real adsorption reactor can be included in the model, because the model would then become too difficult to solve. Therefore some simplifying assumptions have been made. Some of these assumptions can be made without effecting the usefulness of the model. Others are important restrictions of the model. The first three assumptions are the most restrictive ones.

* No radial gradients
  The radial heat transport is mostly fast; consequently only small radial temperature gradients exist. In case of small radial temperature gradients, there will also be only small radial concentration gradients. In this model radial gradients are neglected. Only for reactors with large diameters or with large heat effects, radial gradients can be important.

* Linearised adsorption isotherm
  The adsorption isotherm describes the equilibrium between the fluid phase in the pores $U_s$ and the adsorbed phase $Q$. Normally, the adsorbed concentration is a function of the fluid concentration in the pores and the temperature. In the method used for solving the model equations, the isotherm has to be Laplace transformed with respect to time. Commonly used isotherms are those of Langmuir and Freundlich (Perry, 1985), which are non-linear functions of concentration and temperature. Such functions cannot easily be Laplace transformed. Therefore, a linearised isotherm must be used as an approximation:

$$Q = K_1 + K_2 U_s + K_3 \theta_s$$

This is an important restriction of the method used for solving the model equations.

* Plug flow
  Near the column wall, the packing of solids is less dense than in central portions of the bed, resulting in a separate flow regime near the wall with increased flow rates and increased axial dispersion. Especially for reactors with relatively large particles compared with the column diameter, this effect can be important. For the model, this effect is neglected and plug flow is assumed.

* Pore diffusion limitation
  It is assumed that the pore diffusion is the limiting factor for the adsorption rate in the particles. This means that the mass flow is controlled by the pore diffusion and that the adsorption equilibrium, described by the isotherm, is reached instantaneously, the moment the reactant reaches the surface.
Figure 3.3 Slice of a reactor over which mass and heat balances are calculated
Accumulation in the pores
The mass accumulation in the pores and the heat capacity of the fluid in the pores are generally small compared to the adsorbed concentration and the heat capacity of the solid. They are neglected for this model.

Constant process parameters
Heat capacities, densities and adsorption heat is assumed to be constant with respect to concentrations, temperatures and time.

Wall temperature
The wall temperature is assumed to be uniform and constant.

Pressure drop
The pressure drop across the bed is neglected.

3.6 Development of the Model Equations

Four equations will be developed: the mass balances for the fluid phase and for a particle and the heat balances for the fluid and solid phase. Together with the linearised adsorption isotherm these equations describe the non-isothermal adsorption process.

3.6.1 Mass balance for the fluid phase

Balance for a slice of the reactor (figure 3.3):

\[ \Delta V = \pi R^2 \Delta z \]
\[ \Phi_v = \pi R^2 \varepsilon \nu \]

\[ \text{out} = \text{in} - \text{conversion} - \text{accumulation} \]

\[ \Phi_v C_f \left|_{z=z+\Delta z} \right. - \frac{D_a \pi R^2 \varepsilon}{\delta C_f} \frac{dc_f}{dz} \bigg|_{z=z+\Delta z} + \]

\[ \Delta V (1-\varepsilon) \frac{3}{R_p} D_p \left[ \frac{\delta C_s}{\delta r_p} \right] r_p = R_p = R_p \]

\[ \Phi_v C_f \left|_{z=z} \right. - \frac{D_a \pi R^2 \varepsilon}{\delta C_f} \frac{dc_f}{dz} \bigg|_{z=z} - \Delta V \varepsilon \frac{dc_f}{dt} \quad (3.1) \]
Figure 3.4 Sphere of a particle over which a mass balance is calculated
from (3.1) follows, after division by \( nR^2 \Delta z \cdot \varepsilon 

\[
\begin{align*}
\frac{\partial c_f}{\partial z} + D_a \frac{\partial^2 c_f}{\partial z^2} + \\
\frac{\partial c_f}{\partial t} + \frac{3D_p(1-\varepsilon)}{R_p \cdot \varepsilon} \left[ \frac{\partial c_s}{\partial r_p} \right]_{r_p=R_p} = 0
\end{align*}
\] (3.2)

3.6.2 Mass balance in a particle

Balance for a sphere in a particle (figure 3.4):

\[ \Delta V = 4\pi r_p^2 \Delta r_p \]

\[ \text{out} = \text{in} - \text{conversion} - \text{accumulation} \]

\[
D_p \cdot 4\pi r_p^2 \frac{dcs}{dr_p} \bigg|_{r_p=r_p} = D_p \cdot 4\pi r_p^2 \frac{dcs}{dr_p} \bigg|_{r_p=r_p+\Delta r_p} - \Delta V \frac{dq}{dt}
\] (3.3)

From (3.3) follows, after division by \( 4\pi r_p^2 \cdot \Delta z \cdot \varepsilon \)

\[
\frac{D_p}{r_p^2} \cdot \frac{\partial}{\partial r_p} \left[ r_p^2 \frac{\partial c_s}{\partial r_p} \right]_{t, z} = \frac{\partial q}{\partial t} \left[ r_p, z \right]
\] (3.4)
3.6.3 Heat balance for the fluid phase

Balance for a slice of the reactor (figure 3.3):

\[
\rho_f C_{pf} \Phi_v T_f \left|_{z=z} \right. \frac{dT_f}{dz} \right|_{z=z+\Delta z} - \rho_f C_{pf} \Phi_v T_f \left|_{z=z} \right. \frac{dT_f}{dz} \right|_{z=z} + h_{wf} (T_f - T_{wa1}) \cdot 2\pi R \Delta z \cdot \varepsilon =
\]

\[
\frac{\Delta V \cdot (1 - \varepsilon)}{R_p} h_f (T_s - T_f) - \Delta V \cdot \varepsilon \cdot \rho_f C_{pf} \frac{dT_f}{dt}
\]

After division by \( nR^2 \cdot \Delta z \cdot \varepsilon \) follows:

\[
\begin{align*}
\nu \rho_f C_{pf} \left[ \frac{\delta T_f}{\delta z} \right]_t - \lambda_{fa} \left[ \frac{\delta^2 T_f}{\delta z^2} \right]_t + \frac{2 \cdot h_{wf}}{R_p} (T_f - T_{wa1}) + \\
\rho_f C_{pf} \left[ \frac{\delta T_f}{\delta z} \right]_t = h_f \cdot \frac{3 (1 - \varepsilon)}{R_p} \cdot \varepsilon \cdot (T_s - T_f)
\end{align*}
\]

(3.6)
3.6.4 Heat balance for the solid phase

Balance for a slice of the reactor (figure 3.3):

\[
\Delta V \cdot (1-\varepsilon) \frac{\Delta T_s}{R_p} \cdot h_f \cdot (T_s - T_f) - \lambda_{sa} \cdot nR^2 \cdot (1-\varepsilon) \cdot \frac{dT_s}{dz} \bigg|_{z=z+\Delta z} \\
+ h_{ws} \cdot (T_s - T_{walls}) \cdot 2nR\Delta z \cdot (1-\varepsilon) =
\]

\[
- \lambda_{sa} \cdot nR^2 \cdot (1-\varepsilon) \cdot \frac{dT_s}{dz} \bigg|_{z=z} + (-\Delta H) \cdot (1-\varepsilon) \cdot \frac{dq}{dt} \\
- \Delta V \cdot \rho_s \cdot C_{ps} \cdot (1-\varepsilon) \cdot \frac{dT_s}{dt}
\]

After division by \( nR^2 \cdot \Delta z \cdot (1-\varepsilon) \) follows:

\[
\frac{3}{R_p} \cdot (T_s - T_f) - \lambda_{sa} \cdot \left[ \frac{\delta^2 T_s}{\delta z^2} \right]_t + \frac{2 \cdot h_{ws}}{R} \cdot (T_s - T_{walls}) \\
+ \rho_s \cdot C_{ps} \cdot \left[ \frac{\delta T_s}{\delta t} \right]_z = (-\Delta H) \cdot \frac{\delta q}{\delta t} = (-\Delta H) \cdot \frac{3}{R_p} \cdot \frac{\delta C_s}{\delta r_p} \bigg|_{r_p=R_p}
\]

(3.8)

3.6.5 Boundary and initial conditions

* Two boundary conditions for the place in the bed

For the second partial derivatives with respect to the place, two boundary conditions are needed:

1 - The mass balance for the cross section of the column at \( z=0 \) is:

\[
- D_a \cdot nR^2 \cdot \varepsilon \frac{\delta C_f}{\delta z} \bigg|_{z=0^+} + \Phi_v \cdot C_f \bigg|_{z=0^+} = \Phi_v \cdot C_f \bigg|_{z=0^-}
\]
\[ \frac{\delta c_f}{\delta z} \bigg|_{z=0^+} = \frac{v}{D_a} \left[ c_f \bigg|_{z=0^+} - c_f \bigg|_{z=0^-} \right] \]

Figure 3.5 Scheme of a closed (a) and an open (b) reactor entrance

\[ \frac{\delta c_f}{\delta z} \bigg|_{z=L} = 0 \]

\[ c_f = c_0 \]

Figure 3.6 Scheme of a closed (a) and an open (b) reactor exit
This can be written as:

\[ \frac{\partial C_f}{\partial z} \bigg|_{z=0^+} = \frac{v}{D_a} \left[ C_f \bigg|_{z=0^+} - C_f \bigg|_{z=0^-} \right] \]  \hspace{1cm} (3.9)

Analogous for the fluid temperature:

\[ \frac{\partial T_f}{\partial z} \bigg|_{z=0^+} = \frac{v \cdot \rho_f \cdot C_p_f}{\lambda_f} \left[ T_f \bigg|_{z=0^+} - T_f \bigg|_{z=0^-} \right] \]  \hspace{1cm} (3.10)

It is assumed that there is no heat transfer to the wall at the entrance, therefore:

\[ \frac{\partial T_a}{\partial z} \bigg|_{z=0^+} = 0 \]  \hspace{1cm} (3.11)

Boundary condition (3.9) is different from that of Chen and Hsu (1987). They assume an open system at the entrance, that is, there is no wall at \( z=0 \) that prevents dispersion to that direction (figure 3.5). From \( z=0 \) to \( z=L \), the column is filled with porous particles. Before \( z=0 \), the column is filled with inert particles. Especially for systems with large axial dispersion effects, a system that is open at the entrance differs significantly from a closed system.

2 - A mass balance for the cross section at the end of a closed column (figure 3.6) would give as a boundary condition that the derivative with respect to the place at the end of the bed is zero. However, for finding the solution of the model equations it is easier to assume an open tube end. In that case the boundary conditions are:

\[ C_f \bigg|_{z \to \infty} = 0 \]  \hspace{1cm} (3.12)

\[ T_f \bigg|_{z \to \infty} = 0 \]  \hspace{1cm} (3.13)

\[ T_s \bigg|_{z \to \infty} = 0 \]  \hspace{1cm} (3.14)

The difference between an open and a closed reactor exit is only significant when diffusion and dispersion effects are large and when the tube is small.

* Two boundary conditions for the place in the particle

For the second partial derivative of the fluid concentration in the particles with respect to the particle radius two boundary conditions are needed:

1 - From reasons of symmetry follows that the derivative with respect to the particle radius at the center of the particle will be zero:
2. From the mass balance for a sphere at $r = R_p$ follows:

$$\frac{\partial c_s}{\partial r_p} \bigg|_{r_p = 0} = 0 \quad (3.15)$$

$$\frac{\partial c_s}{\partial r_p} \bigg|_{r_p = R_p} = \frac{k_f}{D_p} (c_f - c_s) \bigg|_{r_p = R_p} \quad (3.16)$$

* Initial conditions

Initially all concentrations are assumed to be zero:

$$c_f \bigg|_{t=0} = 0 \quad c_s \bigg|_{t=0} = 0 \quad q \bigg|_{t=0} = 0$$

(3.17), (3.18), (3.19)

The condition that the adsorbed concentration $q$ is zero at $t=0$, means that the value of $K_i$ in the linearized isotherm (paragraph 3.5) would always be zero.

The initial temperatures are equal to the wall temperature:

$$T_f \bigg|_{t=0} = T_{wa} \quad T_s \bigg|_{t=0} = T_{wa}$$

(3.20), (3.21)

3.6.6 Dimensionless Constants

In the model equations described above, 27 different variables are used:

$$t \quad v \quad z \quad L \quad R \quad r_p \quad R_p \quad c_f \quad c_s \quad q \quad c_0$$

$$T_f \quad T_s \quad T_w \quad T_{wa} \quad D_a \quad D_p \quad (\rho_f \cdot C_p_f) \quad (\rho_s \cdot C_p_s)$$

$$\lambda_f \quad \lambda_s \quad k_f \quad h_f \quad h_{wf} \quad h_{ws} \quad -\Delta H \quad \varepsilon$$

in the S.I. units kg, m, s, K and mole. 27 variables in 5 units leads to 27-5=22 independent dimensionless numbers. The following are chosen:

$$\tau = \frac{t \cdot v}{L} \quad \alpha = \frac{L}{R} \quad \beta = \frac{R}{R_p}$$

$$\chi = \frac{z}{L} \quad \eta = \frac{r_p}{R_p}$$

$$U_f = \frac{c_f}{c_0} \quad U_s = \frac{c_s}{c_0} \quad Q = \frac{q}{c_0}$$
3.6.7 Dimensionless Model Equations

With these dimensionless numbers the model equations can be written as:

Fluid mass balance

\[
\left[ \frac{\partial U_f}{\partial x} \right]_t - \frac{1}{\text{Pe}(m,a)} \left[ \frac{\partial^2 U_f}{\partial x^2} \right]_t + \left[ \frac{\partial U_f}{\partial \tau} \right]_x + \frac{1}{\text{Pe}(m,s)} \cdot 3.\mu \left[ \frac{\partial U_s}{\partial \eta} \right]_{\eta=1} = 0 \quad (3.22)
\]

Particle mass balance

\[
\left[ \frac{\partial Q}{\partial \tau} \right]_{\eta,x} = \frac{1}{\text{Pe}(m,s)} \left[ \frac{\partial^2 U_s}{\partial \eta^2} + \frac{2}{\eta} \frac{\partial U_s}{\partial \eta} \right]_{\tau,x} \quad (3.23)
\]

Isotherm

\[
Q = K_1 + K_2 \cdot U_s + K_3 \cdot \Theta_s \quad (3.24)
\]
Fluid heat balance

\[
\frac{\partial \Theta_f}{\partial x} \tau - \frac{1}{\text{Pe}(h,f)} \frac{\partial^2 \Theta_f}{\partial x^2} \tau + \Theta_f \cdot \dot{W}_f \cdot \frac{2}{\text{Pe}(h,f)} + \frac{\partial \Theta_f}{\partial \tau} \xrightarrow{\text{x}} - \frac{3 \cdot \text{Bi}(h)}{\text{Pe}(h,s)} \cdot \Phi \cdot \mu \cdot (\Theta_s - \Theta_f) = 0 \quad (3.25)
\]

Solid heat balance

\[
- \frac{1}{\text{Pe}(h,s)} \frac{\partial^2 \Theta_s}{\partial x^2} \tau + \Theta_s \cdot \dot{W}_s \cdot \frac{2}{\text{Pe}(h,s)} + \frac{\partial \Theta_s}{\partial \tau} \xrightarrow{\text{x}} + \frac{3 \cdot \text{Bi}(h)}{\text{Pe}(h,s)} \cdot (\Theta_s - \Theta_f) - \frac{3 \cdot \Gamma}{\text{Pe}(m,s)} \frac{\partial U_s}{\partial \eta} \xrightarrow{\eta=1} = 0 \quad (3.26)
\]

Boundary conditions

Fluid mass balance

\[
\frac{\partial U_f}{\partial x} \xrightarrow{x=0^+} = \text{Pe}(m,a) \begin{bmatrix} U_f \xrightarrow{x=0^+} - U_f \xrightarrow{x=0^-} \end{bmatrix} \quad (3.27)
\]

\[
U_f \xrightarrow{x \to \infty} = 0 \quad U_f \xrightarrow{\tau=0} = 0 \quad (3.28), (3.29)
\]

Particle mass balance

\[
\frac{\partial U_s}{\partial \eta} \xrightarrow{\eta=0} = 0 \quad (3.30)
\]

\[
\frac{\partial U_s}{\partial \eta} \xrightarrow{\eta=1} = \text{Bi}(m) \begin{bmatrix} U_f - U_s \xrightarrow{\eta=1} \end{bmatrix} \quad (3.31)
\]
\( Q \bigg|_{\tau=0} = 0 \quad U_s \bigg|_{\tau=0} = 0 \quad (3.32), (3.33) \)

**Fluid heat balance**

\[
\frac{\partial \theta_f}{\partial x} \bigg|_{x=0^+} = \text{Pe}(h,f) \left[ \theta_f \bigg|_{x=0^+} - \theta_f \bigg|_{x=0^-} \right] \quad (3.34)
\]

\( \theta_f \bigg|_{x \to \infty} = 0 \quad \theta_f \bigg|_{\tau=0} = 0 \quad (3.35), (3.36) \)

**Solid heat balance**

\[
\frac{\partial \theta_s}{\partial x} \bigg|_{x=0^+} = 0 \quad \theta_s \bigg|_{x \to \infty} = 0 \quad (3.37), (3.38)
\]

\( \theta_s \bigg|_{\tau=0} = 0 \quad (3.39) \)

### 3.7 Applicability of the Model

The model can be used for adsorption and reaction processes in fixed-bed reactors in which the following mechanisms take place:

* **Axial fluid phase diffusion and dispersion**
* **Mass transfer resistance through the film around the solid phase**
* **Pore diffusion**
* **Heat effects of the adsorption or reaction process**
* **Axial heat conduction of the fluid and solid phase**
* **Heat transfer resistance of the film around the solid phase**
* **Heat transfer from the fluid and solid phase to the wall**

Both for adsorption and reaction processes there are some important restrictions:

**Restrictions on adsorption processes**

* At the surface of the porous solid the fluid phase and the solid phase have to be in equilibrium.
* This equilibrium between the fluid and solid phase must be described by a linearised isotherm, \( Q = K_1 + K_2 * U_s + K_3 * \theta_s \).
Restrictions on reaction processes

The model has been basically developed for adsorption processes, but can be used for reaction processes under the following conditions:

* The reaction must be an equilibrium reaction and this equilibrium must be described by the linearised relation \( Q = K_1 + K_2 U_s + K_3 \theta_s \). In this case \( Q \) is the reaction product and \( U_s \) is the reactant.

* As for adsorption processes, the pore diffusion has to be the limiting factor for the reaction rate in the particles. This means that the equilibrium between the reactants at the surface must be reached instantaneously.

In paragraph 3.5 some other simplifying assumptions were made, but those are mostly of minor importance.
CHAPTER 4

MATHEMATICAL METHODS

4.1 The Fourier and Laplace Transform (Oppenheim and Willsky, 1983)

The Laplace transform of a general function $f(t)$ is defined as

$$F(s) = \int_{0^+}^{+\infty} f(t)\exp(-st)dt,$$  \hspace{1cm} (4.1)

if this integral exists. The complex variable $s$ is of the form $s = a+i\omega$, with $a$ and $\omega$ the real and imaginary parts, respectively. The Fourier Transform of a function $f(t)$ is defined as:

$$F(i\omega) = \int_{-\infty}^{+\infty} f(t)\exp(-i\omega t)dt,$$ \hspace{1cm} (4.2)

So, for a function that is zero for $t<0^+$, the Fourier Transform is equal to the Laplace Transform, when $s=i\omega$. The Laplace transform also bears a straightforward relationship to the Fourier transform when the complex variable $s$ is not purely imaginary. To see this relationship, consider $F(s)$ as specified in equation (4.1) with $s$ expressed as $s = a+i\omega$, so that

$$F(a+i\omega) = \int f(t)\exp(-(a+i\omega)t)dt$$ \hspace{1cm} (4.3)

or

$$F(a+i\omega) = \int [f(t)\exp(-at)]\exp(-i\omega t)dt$$ \hspace{1cm} (4.4)

We recognize the right-hand side of equation (4.4) as the Fourier transform of $f(t)\exp(-at)$; that is, the Laplace transform of $f(t)$ can be interpreted as the Fourier transform of $f(t)$ after multiplication by a real exponential function. The real exponential $\exp(-at)$ may be decaying or growing in time, depending on whether $a$ is positive or negative.

The Fourier transform does not exist for all functions $f(t)$. The Laplace transform may exist for some $a$-values and not for others. Therefore in specifying the Laplace transform of a function, both the function and the range of values of $s$ for which this expression is valid, are required. The range of values of $s$ for which the integral in equation (4.1) converges is referred to as the region of convergence (ROC) of the Laplace transform.
If the Laplace transform of a function is a ratio of polynomials in the complex variable $s$, that is, of the form

$$F(s) = \frac{N(s)}{D(s)} \quad (4.5)$$

where $N(s)$ and $D(s)$ are the numerator and denominator polynomial, $F(s)$ is referred to as rational. $F(s)$ will be rational whenever $f(t)$ is a linear combination of real or complex exponentials, or if $f(t)$ is a result of a linear constant coefficients differential equation. Except for a scale factor, the numerator and denominator polynomials in a rational Laplace transform can be specified by their roots; thus, marking the location of the roots of $N(s)$ and $D(s)$ in the $s$-plane provides a convenient pictorial way of describing the Laplace transform. For rational Laplace transforms, the roots of the numerator polynomial are commonly referred to as the zeros of $F(s)$ since for those values of $s$, $F(s)$ equals zero. The roots of the denominator polynomial are referred to as the poles of $F(s)$, and for those values of $s$, $F(s)$ becomes unbounded.

The inverse Fourier transform is defined as

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} F(\omega) \exp(i\omega t) d\omega \quad (4.6)$$

and the inverse Laplace transform is defined as

$$f(t) = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} F(s) \exp(st) ds \quad (4.7)$$

The contour of integration is a straight line in the complex plane, parallel to the $i\omega$-axis and determined by any value of $a$ so that $F(a+i\omega)$ converges. When $t=0$, the inversion integral has the value $f(O^+)$, and when $t<0$, it has the value zero. The formal evaluation of this integral for a general $F(s)$ requires the use of contour integration in the complex plane, which will be discussed later. However, the inverse Laplace transform can often be easily evaluated by decomposing $F(s)$ into a linear combination of simpler terms, the inverse transform of each of which can be recognized.
4.2 Complex Integration and Residues (Churchill, 1958)

Cauchy's integral theorem states that if $F(s)$ is analytic at all points interior to and on a closed contour $C$, then

$$\int_{C} F(s)ds = 0 \quad (4.8)$$

A function $F$ is analytic at a point $s_0$ if its derivative $F'(s)$ exists at each point in some neighbourhood of $s_0$.

If however, $F(s)$ has an isolated singularity at $s=s_0$, and $s_0$ lies in the interior of $C$, then the integral (4.8) can be non-zero. About an isolated singular point $s_0$ the function can be represented by the so called Laurent series (Churchill, 1958):

$$F(s) = \ldots + \frac{A_{-2}}{(s-s_0)^2} + \frac{A_{-1}}{s-s_0} + A_0 + A_1(s-s_0) + A_2(s-s_0)^2 + \ldots \quad (0 < |s-s_0| < r_0) \quad (4.9)$$

where $r_0$ is the radius of the neighbourhood in which $F$ is analytic, except at $s_0$. For a simple pole, all terms $A_{-n}$ ($n=2,\ldots,\infty$) are zero, thus

$$\lim_{s \to s_0} (s-s_0)F(s) = A_{-1} = \frac{1}{2\pi i} \int_{C} F(s)ds \quad (4.10)$$

This is called the residue of $F$ at the isolated singular point $s_0$.

The residue theorem (Kreyszig, 1983) states that if $F(s)$ is a function which is analytic inside a simple closed path $C$ and on $C$, except for finitely many singular points $s_1, s_2, \ldots, s_n$ inside $C$, then

$$\int_{C} F(s)ds = 2\pi i \sum_{i=1}^{n} \text{Res}_i F(s) \quad (4.11)$$

the integral being taken in the counterclockwise sense around the path $C$. The residues are those calculated by equation (4.10) for simple poles.

For a pole of $m^{th}$ order at $s=s_0$, i.e. the Laurent series starts from $A_{-m}$, can be shown that (Kreyszig, 1983).

$$\text{Res}_{s=s_0} F(s) = \frac{1}{(m-1)!} \lim_{s \to s_0} \frac{d^{m-1}}{ds^{m-1}}[(s-s_0)^mF(s)] \quad (4.12)$$
Figure 4.1 Integration path in the Laplace domain
4.3 Inverse Laplace Transformation by the Method of Residues
(Churchill, 1958)

A function $F$ is on the order of $s^k$ as $|s| \to \infty$ in a specified
part of the $s$-plane, if positive numbers $M$ and $r_0$ exist such
that $|s^{-k}F(s)| < M$ there whenever $|s| > r_0$; that is, when $|s|$ is
sufficiently large,

$$|F(s)| < M|s|^k$$  \hspace{1cm} (4.13)

Let us now consider a function $F(s)$ that is analytic for all
finite values of the complex variable $s$ except for a set of
isolated singular points $s_1, s_2, \ldots$, confined to some left
half plane $\Re(s) < \alpha$. We assume also that $F(s)$ satisfies the
following conditions under which its inversion integral along
the line $a=\mu$ converges to the inverse transform $f(t)$.

The following theorem gives conditions on a function $F$ that are
sufficient to ensure that $L^{-1}\{|F(s)|$ exists:

**Theorem:** Let $F$ be a function of the complex variable $s$ that is
analytic and on the order of $s^{-k}$ for all $s (s=a+i\omega)$ over a half
plane $\alpha \leq \alpha$, where $k>1$; also let $F(a)$ be real when $a\geq \alpha$. Then for
all real $t$ the inversion integral of $F(s)$ along any line $a=\mu$, where $\mu \geq \alpha$, converges to a real-values function $f$ that is
independent of $\mu$,

$$f(t) = L^{-1}\{F(s)\} = \frac{1}{2\pi i} \int_{\mu-i\infty}^{\mu+i\infty} \exp(ts)F(s)ds \quad (|t|<\infty)$$  \hspace{1cm} (4.14)

$f(t)$ can then be represented by a series, finite or infinite,
depending on the number of singular points. Note that $\mu$ can be
chosen freely, as long as $\mu$ is greater than $\alpha$.

Since $\exp(ts)$ is an analytic function for all finite $s$, the
singular points $s=s_\alpha$ of $F(s)$ are the singular points of the
integrand $\exp(ts)F(s)$ of the inversion integral. Let $\rho_n(t)$
denote the residue of the integrand, for any fixed $t$, at the
isolated singular point $s_n$:

$$\rho_n(t) = \text{residue of } \exp(ts)F(s) \text{ at } s = s_n$$  \hspace{1cm} (4.15)

According to the residue theorem, the integral of $\exp(ts)F(s)$
around a path enclosing the points $s_1, s_2, \ldots, s_N$ has the value
$2\pi i[\rho_1(t) + \rho_2(t) + \ldots + \rho_N(t)]$. Let the path be made up of the
line segment joining the points $\mu-i\beta_N, \mu+i\beta_N$, and some contour
$C_N$, beginning at the second and ending at the first of these
two points, and lying in the half plane $\alpha \leq (\text{figure 4.1}). Then

$$\frac{1}{2\pi i} \int_{\mu-i\beta_N}^{\mu+i\beta_N} \exp(ts)F(s)ds + \frac{1}{2\pi i} \int_{C_N} \exp(ts)F(s)ds = \sum_{n=1}^{N} \rho_n(t)$$  \hspace{1cm} (4.16)

As $\beta_N \to \infty$, the value of the first integral here tends to
$L^{-1}\{|F(s)\}$, since the inversion integral is the limit of the
corresponding integral involving $\beta$, as $\beta \to \infty$ in any manner. Let
the numbers $\beta_n$ (N=1,2,...) be selected so that $\beta_n \to \infty$, and let the curves $C_n$ together with the line $a=\mu$ enclose the points $s_1,s_2,...,s_N$, if the number of singular points is infinite. If the number is finite, let all of them be enclosed when $N$ is greater than some fixed number. Then, if $F(s)$ and $C_n$ satisfy additional conditions, which will be discussed later, under which

$$\lim_{N \to \infty} \frac{1}{2\pi i} \int_{C_n} \exp(ts)F(s)ds = 0 \quad (4.17)$$

it follows, by letting $N \to \infty$ in equation (4.16), that

$$L^{-1}\{F(s)\} = \sum_{n=1}^{\infty} \rho_n(t) \quad (4.18)$$

or by a finite series in case the number of singular points is finite. The series on the right is necessarily convergent because the limit, as $N \to \infty$, of the left-hand member of equation (4.16) exists.

Since the inversion integral represents $f(t)$ by hypothesis, the inverse transform of $F(s)$ is represented as the series of residues of $\exp(ts)F(s)$:

$$f(t) = \sum_{n=1}^{\infty} \rho_n(t) \quad (4.19)$$

It is sometimes convenient to use the series representation (4.19) directly, without regard to conditions under which the inversion integral represents $f(t)$ and the integral over $C_n$ tends to zero. The function $f$ so obtained may be such that its transform can be shown to be $F(s)$, or such that it satisfies all conditions in a problem which solution was sought by the transformation method.

For the application of this method we have to know under what conditions the integrals of $\exp(ts)F(s)$ over certain useful contours $C_n$ tend to zero when $N \to \infty$, as assumed above in equation (4.17). The following theorem can be proven:

**Theorem:** Let $F$ be analytic everywhere except for isolated singular points $s_n$ (n=1,2,...) in a half plane $a<\mu$ and such that its inversion integral along the line $a=\mu$ represents the inverse Laplace transform $f(t)$ of $F(s)$. On contours $C_n$ (N=1,2,...) in the left hand plane $a<\mu$, let $F$ satisfy the order condition $|F(s)|<M|s|^{-k}$ where $M$ and $k$ are positive constants independent of $N$, and $C_n$ is either (a) a rectangular path, (b) circular arcs $|s|=(\beta_n^2+\mu^2)^{1/2}$, $a=\mu$, or (c) parabolic arcs $\beta_n^2=4\mu(\mu+a\mu)$, $a=\mu$, where $\beta_n \to \infty$ as $N \to \infty$. Then whenever $t>0$, the series of residues $\rho_n(t)$ of $\exp(ts)F(s)$ at $s_n$ converges to $f(t)$ (eqn. 4.19), if its terms corresponding to points $s_n$ within the ring between successive paths $C_n$ and $C_{n+1}$ are grouped as a single terms of the series. Also, if $k>1$ and $L^{-1}\{F\}$ represents $\frac{1}{2}f(+0)$ when $t=0$, then
Figure 4.2 Graphical development of the discrete Fourier transform (Churchill, 1958)
4.4 The Discrete Fourier Transform

Brigham (1974) gives a clear explanation of the way the discrete Fourier transform can be developed from the continuous Fourier transform:

Consider the example function \( h(t) \) and its Fourier transform \( H(f) \) illustrated in figure 4.2(a). It is desired to modify this Fourier transform pair in such a manner that the pair is amenable to digital computer computation. This modified pair, termed the discrete Fourier transform is to approximate as closely as possible the continuous Fourier transform.

To determine the Fourier transform of \( h(t) \) by means of digital analysis techniques, it is necessary to sample \( h(t) \). Sampling is accomplished by multiplying \( h(t) \) by the sampling function illustrated in figure 4.2(b). The sample interval is \( T \). The sampled function \( h(t) \) and its Fourier transform are illustrated in figure 4.2(c). This Fourier transform pair represents the first modification to the original pair which is necessary in defining a discrete transform pair. According to the sampling theorem, there is no loss of information as a result of sampling if \( h(t) \) is sampled at a frequency of at least twice the largest frequency component of \( h(t) \). If the function \( h(t) \) is not band-limited, i.e., \( H(f) \neq 0 \) for some \( |f| > f_c \), then sampling will introduce aliasing as illustrated in figure 4.2(c). To reduce this error we have only one recourse, and that is to sample faster.

The Fourier transform pair in figure 4.2(c) is not suitable for machine computation because an infinity of samples of \( h(t) \) is considered. It is necessary to truncate the sampled function \( h(t) \) so that only a finite number of points, say \( N \), are considered. The rectangular or truncation function and its Fourier transform are illustrated in figure 4.2(d). The product of the infinite sequence of impulse functions representing \( h(t) \) and the truncation function yields the finite length time function illustrated in figure 4.2(e). Truncation introduces the second modification of the original Fourier transform pair. This effect is to convolve the aliased frequency transform of figure 4.2(c) with the Fourier transform of the truncation function, figure 4.2(d). As shown in figure 4.2(e) the frequency transform now has a ripple to it. This effect has been accentuated in the illustration for emphasis. This effect can be reduced by taking a longer truncation function.

The modified transform pair of figure 4.2(e) is still not an acceptable discrete Fourier Transform pair because the frequency transform is a continuous function. For machine computation, only sample values of the frequency function can be computed. It is necessary to modify the frequency transform.
by the frequency sampling function illustrated in figure 4.2(f). The frequency sampling interval is $1/T_0$.

The discrete Fourier transform pair of figure 4.2(g) is acceptable for the purpose of digital machine computation since both the time and frequency domains are represented by discrete values. As illustrated in figure 4.2(g), both the original time function and the original Fourier transform $H(f)$ are approximated by $N$ samples. These $N$ samples define the discrete Fourier transform pair and approximate the original Fourier transform pair. Note that sampling in the time domain resulted in a periodic function of frequency; sampling in the frequency domain resulted in a periodic function of time. Hence, the discrete Fourier transform requires that both the original time and frequency functions be modified such that they become periodic functions.

### 4.5 Inverse Laplace Transformation by Applying the Fourier Transform

Hsu and Dranoff (1987) give a good explanation why the discrete Fourier Transform can be used for inverse Laplace transforms. Using the trapezoidal rule approximation to equation (4.7), with $\omega = k\pi/T$ and $\Delta \omega = \pi/T$, we obtain:

$$f(t) = \frac{\exp(at)}{2T} \left[ \sum_{k=-\infty}^{\infty} F(a + ik\pi/T) \cdot \exp(ik\pi t/T) \right]$$  \hspace{1cm} (4.21)

Assuming $t=j\Delta T$, equation (4.21) can be put into the following form, because of periodicity of a complex exponential:

$$f(j\Delta T) = \frac{\exp(a j\Delta T)}{2T} \sum_{k=0}^{N-1} A(k) \cdot \exp(i2\pi jk/N)$$  \hspace{1cm} (4.22)

where

$$A(k) = \sum_{n=-\infty}^{+\infty} F[a + i\pi/T.(k + nN)]$$  \hspace{1cm} (4.23)

with $N\Delta T = 2T$, and $j=0,1,2,\ldots,N-1$

The expressions of equations (4.22) and (4.23) may be simplified by selecting $N/2 > T\omega_{max}/n$, where $\omega_{max}$ is the largest frequency for which $F(a+i\omega_{max})$ is less than a desired value. Thus, equations (4.22) and (4.23) can be reduced to
Figure 4.3 Effect of the number of sample points and the time period on the inverse transform: (a) reference, $N=64$, $2T=30000$; (b) not enough points, $N=8$, $2T=30000$; (c) time period too small, $N=64$, $2T=10000$. Laplace functions are differentiated.
\[ f(j\Delta T) = \frac{\exp(aj\Delta T)}{2T} \sum_{k=0}^{N-1} F(a + ik/T) \exp(i2\pi jk/N) \]

where \( \Delta T = 2T/N \). The result of this approximation is a periodic function \( f(t) \) with period 2T; however, we are only interested in the result from 0 to 2T.

Two properties of \( F(a + ik/T) \) should be noted:

1. For a real function, the discrete Fourier transforms \( F(a+i\omega) \) and \( F(a-i\omega) \) are complex conjugates.
2. As explained in the previous paragraph, \( F(a+i\omega) \) is periodic over \( \omega \) with period \( 2\pi/\Delta T \), i.e. \( F(a+i\omega) = F(a+i(\omega+2\pi/\Delta T)) \).

So, \( \text{Re}[F(a+i\omega)] \) (the real part of the complex frequency function) is an even function and \( \text{Im}[F(a+i\omega)] \) is an odd function. Therefore, only the values of \( F(a+ink/T) \) for \( k=0 \) to \( N/2 \) must be computed. After calculation of the real part from \( k=0 \) to \( N/2 \), the values for \( k=N/2+1 \) to \( N \) can be obtained by folding the function about the sample point at \( k=N/2 \). The imaginary part for \( k=N/2+1 \) to \( N \) can be calculated from the values for \( k=0 \) to \( N/2 \) by folding about the sample value at \( N/2 \), and also changing the sign. To preserve symmetry for the imaginary part the value at \( k=N/2 \) must be set to zero.

For those problems where the poles of \( F(s) \) lie on the left-hand side of the origin, the \( a \)-value can be assumed to equal zero. Equation (4.24) then simplifies to:

\[ f(j\Delta T) = \frac{1}{2T} \sum_{k=0}^{N-1} F(ik/T) \exp(i2\pi jk/N) \]  \hspace{1cm} (4.25)

The Fast Fourier Transform algorithm is a very fast method for calculating formula (4.25), especially when \( N \) is a power of 2. This method is extensively described by Brigham (1974). The program for this algorithm is available in most computer libraries.

Formula (4.24) can be calculated by applying the FFT to \( F(a+ik/T) \) and multiplying the result by \( \exp(aj\Delta T) \). Theoretically, the \( a \)-value can be chosen freely, as long as \( a \) is greater than the greatest real part of the singularities. However, numerical problems restrict this choice.

The effects of the number of points that is used for sampling and the time period for which the inverse transform is calculated are illustrated in figure 4.3. The number of points (\( N \)) must be chosen such that doubling of that number does not change the calculated curves significantly. In figure 4.3(b), the number of points is chosen too small. The time period (2T)
Figure 4.4 Effect of an $a$-value that is too high: strong oscillations for high $\tau$-values. $N=64$, $2T=30000$, $a=0.002$

Figure 4.5 Effect of an $a$-value that is too small: translation to higher values. $N=64$, $2T=30000$, $a=0.00001$

Figure 4.6 Example of a function for which differentiation does not give correct results. $N=64$, $2T=30000$. 
must be chosen such that the function has reached its stationary value. In figure 4.2(c), the time period is chosen too small.

The examples of figures 8.2-8.6 are concentration breakthrough curves with the parameters: \( \text{Pe}(m,s) = 2; \text{Pe}(m,a) = 20; \text{Bi}(m) = 10000; \mu = 1.5; K_2 = 5000. \)

The choice of the a-value

Laplace transforms of concentration breakthrough curves have always a singularity at the origin. Consequently, the a-value has to be chosen positive. There are two important factors that restrict the range of a-values. If the a-value is too high, the growing exponential \( \exp(\alpha \Delta t) \) amplifies inaccuracies (figure 4.4). On the other hand, if the a-value is too close to the singularity at the origin, the inversed functions are translated parallel to the function value-axis to higher values (figure 4.5). Therefore it would be easy to have a method that could avoid the choice of the a-value. There are two major possibilities:

1 - Differentiate \( F(s) \) by multiplying it by \( s \). The singularity at the origin is now eliminated. All the real parts of the singularities are negative, and so, the a-value can be chosen zero. Inverse transformation of this function gives the differentiated time-function, which has to be integrated for the correct result. Sometimes, differentiation does not give correct results (figure 4.6)

2 - \( F(s) \) can be written as

\[
F(s) = \frac{A}{s} + \left[ F(s) - \frac{A}{s} \right]
\]

We want \( A \) to be chosen such that the function \( F(s) - \frac{A}{s} \) has no singularity at the origin. In that case, the a-value for inverse transformation of \( F(s) - \frac{A}{s} \) can be chosen zero. \( \frac{A}{s} \) can easily be inverse transformed. From the final value theorem (Oppenheim and Willsky, 1983)

\[
\lim_{t \to \infty} f(t) = \lim_{s \to 0} s \cdot F(s)
\]

(4.27)

can be deduced that this is the case when

\[
A = \lim_{t \to \infty} f(t)
\]

(4.28)

This is the stationary value of the function \( f(t) \), also referred to as \( f(\infty) \). Inverse transformation of equation (4.26) gives:

\[
f(t) = f(\infty) + \left[ F(s) - \frac{f(\infty)}{s} \right]^{-L}
\]

(4.29)
Figure 4.7 Effect of tapering: (a) without tapering; (b) with tapering. $N=64$, $2T=30000$. 
By subtracting \( f(\omega)/s \) from \( F(s) \), the singularity of \( F(s) \) at the origin is eliminated, and so, the \( a \)-value can be chosen zero.

**Tapering of \( \text{Im}(F(s)) \)**

Because the imaginary part of \( F(s) \) is calculated for a limited range of \( \omega \)-values, and because the imaginary part of \( F(s) \) is an odd function, there will be a discontinuity in \( \text{Im}(F(s)) \) at the point for \( k = N/2 \). Only in those cases where \( \text{Im}(F(s)) \) is calculated over a long \( \omega \)-range, such that \( \text{Im}(F(s)) \) has become zero for the largest \( \omega \)-values, there is no discontinuity. A discontinuity at a high frequency causes oscillations of the time function (figure 4.7). These oscillations can be avoided by tapering the imaginary part of \( F(s) \), for example with a cosine function, such that the discontinuity disappears.

**4.6 More Efficient Use of the Fourier Transform**

As explained in the previous paragraph, the real part of \( F(s) \) is even and the imaginary part of \( F(s) \) is odd. As input for the Fast Fourier routine, a complete period of \( F(s) \) is needed, thus, each point is given twice. Since the imaginary part of the function \( f(t) \) is zero, \( f(t) \) has the same 'degree of freedom' as the input data set. This use of the FFT routine looks inefficient, and indeed, it is. There is a more efficient and faster way, without redundancy, that uses only half the memory size (Press et al. 1987). Therefore, using this method, twice as many points can be used with the same memory limitation.

It can be proven that a discrete Fourier transform of length \( N \) can be written as the sum of two discrete Fourier transforms, each of length \( N/2 \):

\[
F_n = \sum_{k=0}^{N-1} \exp(-2\pi i kn/N) f_k
\]

\[
= \sum_{k=0}^{N/2-1} \exp(-2\pi in(2k)/N) f_{2k} + \sum_{k=0}^{N/2-1} \exp(-2\pi in(2k+1)/N) f_{2k+1}
\]

\[
= \sum_{k=0}^{N/2-1} \exp(-2\pi ink/(N/2)) f_{2k} + \sum_{k=0}^{N/2-1} \exp(-2\pi ink/N) \sum_{k=0}^{N/2-1} \exp(-2\pi ink/(N/2)) f_{2k+1}
\]

\[
= F_n^e + \exp(-2\pi in/N).F_n^o
\]

(4.30)
$F_{n}^{e}$ and $F_{n}^{o}$ are both Fourier transforms of real functions, thus,

$$F_{n}^{e} = rac{F_{N/2-n}}{2} \quad (4.31)$$

$$F_{n}^{o} = rac{F_{N/2-n}}{2} \quad (4.32)$$

From (4.30) follows (with (4.31) and (4.32)):

$$F_{n/2-n} = F_{n/2-n}^{e} + \exp(-2\pi i(N/2-n)/N).F_{n/2-n}^{o}$$

$$= F_{n}^{e*} - \exp(2\pi i n/N).F_{n}^{o*} \quad (4.33)$$

Conjugation of (4.33) gives:

$$F_{n/2-n}^{*} = F_{n}^{e} - \exp(-2\pi i n/N).F_{n}^{o} \quad (4.34)$$

$F_{n}^{e}$ and $F_{n}^{o}$ can be solved from (4.30) and (4.34):

$$F_{n}^{e} = \frac{1}{2}(F_{n} + F_{n/2-n}^{*}) \quad (4.35)$$

$$F_{n}^{o} = \frac{1}{2}\exp(2\pi i n/N).(F_{n} - F_{n/2-n}^{*}) \quad (4.36)$$

The input for the FFT routine is calculated from

$$H_{n} = F_{n}^{e} + iF_{n}^{o} \quad (4.37)$$

with as a result of the inverse transformation:

$$h_{j} = f_{2j} + if_{2j+1} \quad j=0,\ldots,N/2-1 \quad (4.38)$$

The even points of the inverse transform $f(t)$ can be found in the real part of $h(t)$ and the odd points can be found in the imaginary part.

So, the efficiency is achieved by rearrangement of the elements (either $F(s)$ or $f(t)$). In the computer program, the inverse transforms are calculated without this 'trick', in order to keep clarity.
SOLUTION OF THE MODEL EQUATIONS

In chapter 3, the model equations have been deduced, (3.22)-(3.39). This set of partial differential equations can be solved by Laplace transformation with respect to both time ($\tau$) and place ($x$). Laplace transformation with respect to $\tau$ gives a set of partial differential equations in $s$ and $x$. This domain is here being referred to as the first Laplace domain. The Laplace transformation with respect to $x$ will give a set of linear equations in $s$ and $y$ which can be solved. This domain will be referred to as the second Laplace domain.

After solution of the equations in the second Laplace domain, the inverse Laplace transformation with respect to $x$ can be done by the method of residues, which has been explained in paragraph 4.3. The inverse Laplace transformation with respect to $\tau$ must be done numerically. As discussed in paragraph 4.5, the Fast Fourier Transform is a very fast method for the numerical calculation of inverse Laplace Transforms.

5.1 Laplace Transformation with Respect to time and place

In this paragraph, the Laplace transformation of the model equations with respect to both time and place is described in equations (5.1)-(5.21). The result of this transformation is given by equation (5.22).

Laplace transformation with respect to $\tau$ results in functions of $s$. These functions are marked by a dash. Laplace transformation with respect to $x$ results in functions of $y$, marked by a dash and an accent circumflex (^). Substitution of equation (3.24) in equation (3.23) eliminates $Q$:

$$\frac{\partial Q}{\partial \tau} = K_2 \frac{\partial U_s}{\partial \tau} + K_3 \frac{\partial \theta_s}{\partial \tau} = \frac{1}{Pe(m,s)} \left[ \frac{\partial^2 U_s}{\partial \eta^2} + \frac{2 \partial U_s}{\partial \eta} \right] \tau, x$$

(5.1)

Laplace transformation with respect to $\tau$ results in a function of $s$:

$$K_2 \cdot s \cdot \bar{U}_s + K_3 \cdot s \cdot \bar{\theta}_s = \frac{1}{Pe(m,s)} \left[ \frac{\partial^2 \bar{U}_s}{\partial \eta^2} + \frac{2 \partial \bar{U}_s}{\partial \eta} \right] \tau, x$$

(5.2)
The general solution of this differential equation is:

$$\tilde{U}_s = A'(s,x). \exp(-n\sqrt{K_2 \cdot s \cdot Pe(m,s)}) + B'(s,x). \exp(n\sqrt{K_2 \cdot s \cdot Pe(m,s)}) = \frac{K_3}{K_2} \cdot \Theta_s$$  

(5.3)

From boundary condition (3.30)

$$\frac{\partial \tilde{U}_s}{\partial n} \bigg|_{n=0} = 0 \quad \text{follows} \quad \frac{\partial \tilde{U}_s}{\partial n} \bigg|_{n=0} = 0$$

consequently, $A' = -B'$. Substitution in (5.3) gives:

$$\tilde{U}_s = A(s,x). \frac{\sinh(n\sqrt{K_2 \cdot s \cdot Pe(m,s)})}{K_2} - \frac{K_3}{K_2} \cdot \Theta_s$$

(5.4)

Laplace transformation of (5.4) with respect to $x$ results in a function of $y$:

$$\hat{\tilde{U}}_s = \hat{A}(s,y). \frac{\sinh(n\sqrt{K_2 \cdot s \cdot Pe(m,s)})}{K_2} - \frac{K_3}{K_2} \cdot \hat{\Theta}_s$$

(5.5)

differentiation with respect to $n$ for $n=1$ gives

$$\frac{\partial \hat{\tilde{U}}_s}{\partial n} \bigg|_{n=1} = \hat{A}(s,y). (\sqrt{.}) \cosh(\sqrt{.}) - \sinh(\sqrt{.})$$

(5.6)

with $\sqrt{.} = \sqrt{K_2 \cdot s \cdot Pe(m,s)}$

Substitution of equations (5.5) and (5.6) in boundary condition (3.31) gives

$$\hat{A}(s,y). (\sqrt{.}) \cosh(\sqrt{.}) - \sinh(\sqrt{.}) = Bi(m). (\hat{U}_f - \hat{\tilde{A}}(s,y). \sinh(\sqrt{.}) + K_3/K_2 \cdot \hat{\Theta}_s)$$

(5.7)

from which follows:

$$\hat{A} \left[ \frac{\sqrt{.}}{Bi(m)} \cosh(\sqrt{.}) - \sinh(\sqrt{.}) + \sinh(\sqrt{.}) \right] = \hat{U}_f + \frac{K_3}{K_2} \cdot \hat{\Theta}_s$$

(5.8)
By substitution of equation (5.8) in equation (5.5), \( \dot{U}_s \) can be written as a function of \( \dot{U}_f \) and \( \theta_s \):

\[
\begin{align*}
\frac{\dot{U}_s}{\dot{U}_f} = & -\left[ \frac{K_3}{K_2} \frac{\dot{U}_f + \frac{\partial}{\partial s} \theta_s}{\frac{\partial}{\partial x} \theta_s} \right] \left( \frac{\sinh(\eta \sqrt{K_2 s Pe(m,s)})}{\eta} \right) \\
& \left[ \frac{\sqrt{\eta} \cosh(\sqrt{\eta}) - \sinh(\sqrt{\eta})}{B_i(m)} + \sinh(\sqrt{\eta}) \right]^{-1} - \frac{K_3}{K_2} \frac{\dot{U}_f + \frac{\partial}{\partial s} \theta_s}{\dot{U}_f + \frac{\partial}{\partial s} \theta_s} \\
\end{align*}
\]

(5.9)

This is the first equation in the second Laplace domain.

Laplace transformation of equation (3.22) with respect to \( \tau \) gives:

\[
\begin{align*}
\left[ \frac{\partial \dot{U}_f}{\partial \tau} \right]_{\tau} - \left[ \frac{1}{Pe(m,a)} \frac{\partial^2 \dot{U}_f}{\partial x^2} \right]_{\tau} + \\
\left( s \dot{U}_f + \frac{1}{Pe(m,s)} \right) \left( \frac{3}{3.\mu} \frac{\partial \dot{U}_f}{\partial \eta} \right)_{\eta=1} = 0 \\
\end{align*}
\]

(5.10)

Laplace transformation with respect to \( x \):

\[
\left. y \dot{U}_f - \dot{U}_f \right|_{x=0} - \left[ \frac{1}{Pe(m,a)} \left( y^2 \dot{U}_f - y \dot{U}_f \right) \right]_{x=0} - \left[ \frac{\partial \dot{U}_f}{\partial x} \right]_{x=0}
\]

\[
\begin{align*}
\left. s \dot{U}_f + \frac{1}{Pe(m,s)} \right) \left( \frac{3}{3.\mu} \frac{\partial \dot{U}_f}{\partial \eta} \right)_{\eta=1} = 0 \\
\end{align*}
\]

(5.11)

substituting equation (5.6) yields

\[
\dot{A} \left( \sqrt{\eta} \cosh(\sqrt{\eta}) - \sinh(\sqrt{\eta}) \right) \frac{3.\mu}{Pe(m,s)} + \\
\dot{\dot{U}}_f \left( s + y - y^2 / Pe(m,a) \right) = b_0 - \frac{1}{Pe(m,a)} (y b_0 + b_1)
\]

with

\[
\left. b_0 = \dot{U}_f \right|_{x=0} \quad \left. b_1 = \frac{\partial \dot{U}_f}{\partial x} \right|_{x=0}
\]

(5.12)
Substitution of equation (5.8) into equation (5.12) gives:

\[
\frac{\partial}{\partial t} \left[ \frac{-y^2}{\text{Pe}(m,a)} + y + s + \frac{3.\mu \Phi_0}{\text{Pe}(m,s)} \right] + \frac{\partial}{\partial s} \frac{3.\mu \Phi_0}{\text{Pe}(m,s)} K_3 = \frac{1}{\text{Pe}(m,a)} (y.b_0 + b_1)
\]

with

\[
\Phi_0 = \frac{\sqrt{\ldots} \cosh(\sqrt{\ldots}) - \sinh(\sqrt{\ldots})}{\sqrt{\ldots} \cosh(\sqrt{\ldots}) - \sinh(\sqrt{\ldots})} + \sinh(\sqrt{\ldots})
\]

This is the second equation in the second Laplace domain.

Laplace transformation of equation (3.25) with respect to \( \tau \) yields:

\[
\left[ \frac{\partial \Theta_f}{\partial x} \right] - \frac{1}{\text{Pe}(h,f)} \left[ \frac{\partial^2 \Theta_f}{\partial x^2} \right] + \Theta_f . W_f . \frac{2}{\text{Pe}(h,f)} + s. \Theta_f - \frac{3.\text{Bi}(h)}{\text{Pe}(h,s)} . \Phi . \mu . (\Theta_s - \Theta_f) = 0
\]

Laplace transformation with respect to \( x \) gives:

\[
y. \Theta_f - \Theta_f \bigg|_{x=0} - \frac{1}{\text{Pe}(h,f)} \left[ y^2. \Theta_f - y. \Theta_f \bigg|_{x=0} - \frac{\partial \Theta_f}{\partial x} \bigg|_{x=0} \right] + \Theta_f . W_f . \frac{2}{\text{Pe}(h,f)} + s. \Theta_f - \frac{3.\text{Bi}(h)}{\text{Pe}(h,s)} . \Phi . \mu . (\Theta_s - \Theta_f) = 0
\]

equation (5.16) can be written as

\[
\frac{\partial}{\partial t} \left[ s + y - \frac{y^2}{\text{Pe}(h,f)} + W_f . \frac{2}{\text{Pe}(h,f)} + \frac{3.\text{Bi}(h)}{\text{Pe}(h,s)} . \Phi . \mu \right] - \frac{3.\text{Bi}(h)}{\text{Pe}(h,s)} . \Phi . \mu = \frac{1}{\text{Pe}(h,f)} (y.gr_0 + gr_1)
\]

(5.17)
with
\[ g_{f0} = \left. \frac{\partial \theta_f}{\partial x} \right|_{x=0} \quad g_{f1} = \left. \frac{\partial \theta_f}{\partial x} \right|_{x=0} \]

This is the third equation in the second Laplace domain.

Laplace transformation of equation (3.26) with respect to \( \tau \) gives:

\[
- \frac{1}{\text{Pe}(h,s)} \left[ \frac{\partial^2 \theta_s}{\partial x^2} \right] \tau + \left. \frac{\partial \theta_s}{\partial x} \right|_{x=0} \frac{2}{\text{Pe}(h,s)} + s \left. \frac{\partial \theta_s}{\partial x} \right|_{x=0} 
+ \frac{3 \text{Bi}(h)}{\text{Pe}(h,s)} \left( \theta_s - \theta_f \right) - \frac{3 \Gamma}{\text{Pe}(m,s)} \left[ \frac{\partial U_s}{\partial \eta} \right]_{\eta=1} = 0 \tag{5.18}
\]

Laplace transformation with respect to \( x \):

\[
- \frac{1}{\text{Pe}(h,s)} \left[ y^2 \left. \frac{\partial \theta_s}{\partial y} \right|_{y=0} - \left. \frac{\partial \theta_s}{\partial x} \right|_{x=0} \right] + \left. \frac{\partial \theta_s}{\partial x} \right|_{x=0} \frac{2}{\text{Pe}(h,s)} 
+ s \left. \frac{\partial \theta_s}{\partial x} \right|_{x=0} + \frac{3 \text{Bi}(h)}{\text{Pe}(h,s)} \left( \theta_s - \theta_f \right) - \frac{3 \Gamma}{\text{Pe}(m,s)} \left[ \frac{\partial U_s}{\partial \eta} \right]_{\eta=1} = 0 \tag{5.19}
\]

With substitution of equation (5.6) this can be written as

\[
\left. \frac{\partial}{\partial s} \left[ s - \frac{y^2}{\text{Pe}(h,s)} + \left. \frac{\partial \theta_s}{\partial x} \right|_{x=0} \right] \frac{2}{\text{Pe}(h,s)} + \frac{\text{Bi}(h) \cdot 3}{\text{Pe}(h,s)} \right] 
- \left. \frac{\partial \theta_f}{\partial x} \right|_{x=0} \frac{\text{Bi}(h) \cdot 3}{\text{Pe}(h,s)} \right] 
- \frac{3 \Gamma}{\text{Pe}(m,s)} \left( \sqrt{v} \cdot \cosh(\sqrt{v}) \right. 
- \sinh(\sqrt{v}) \right) 
= - \frac{1}{\text{Pe}(h,s)} \left( y \cdot g_{f0} + g_{f1} \right) \tag{5.20}
\]

with
\[ g_{f0} = \left. \theta_s \right|_{x=0} \quad g_{f1} = \left. \frac{\partial \theta_s}{\partial x} \right|_{x=0} \]

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Substitution of equation (5.8) into equation (5.20) gives:

\[
\begin{align*}
- \frac{\vartriangle U_f}{\text{Pe}(m,s)} + \frac{\vartriangle \theta_f}{\text{Pe}(h,s)} &= \frac{3 \vartriangle \Phi_s}{\text{Pe}(m,s)} - \frac{3 \vartriangle \Phi_s}{\text{Pe}(h,s)} + \\
\left[ - \frac{y^2}{\text{Pe}(h,s)} + s + W_s \right] &= \left[ \frac{2}{\text{Pe}(h,s)} + \frac{3 \vartriangle \Phi_s}{\text{Pe}(h,s)} - \frac{3 \vartriangle \Phi_s}{\text{Pe}(m,s)} \cdot \frac{K_3}{\text{Pe}(h,s)} \right] - \frac{1}{\text{Pe}(h,s)} (y g_{s0} + g_{s1}) \text{ (5.21)}
\end{align*}
\]

This is the fourth equation in the second Laplace domain. Only the isotherm (3.24) is not yet transformed. However, this is not necessary because after substitution into equation (3.23), this is the only equation that is a function of \( Q \). Consequently, after inverse transformation of \( \bar{U}_s \) and \( \bar{\theta}_s \), \( Q \) can directly be calculated from \( K_1, K_2, K_3, U_s \) and \( \theta_s \).

The equations (5.9), (5.13), (5.17) and (5.21) form a set of four linear equations of \( U_f, \bar{U}_s, \vartriangle \theta_f, \) and \( \vartriangle \theta_s \). Equation (5.9) is the only one that is a function of \( \bar{\theta}_s \). \( \bar{U}_s \) can thus be calculated after calculation of \( \vartriangle U_f \) and \( \vartriangle \theta_f \) from the other equations, that can be written in matrix notation:

\[
\begin{bmatrix}
A & B & 0 \\
D & E & F \\
0 & H & I
\end{bmatrix}
\begin{bmatrix}
\vartriangle U_f \\
\vartriangle \theta_s \\
\vartriangle \theta_f
\end{bmatrix}
= 
\begin{bmatrix}
R_1 \\
R_2 \\
R_3
\end{bmatrix}
\text{ (5.22)}
\]

with

\[
A = \frac{- y^2}{\text{Pe}(m,a)} + y + s + \frac{3 \vartriangle \Phi_s}{\text{Pe}(m,s)} \text{ (5.22a)}
\]

\[
B = \frac{3 \vartriangle \Phi_s}{\text{Pe}(m,s)} \cdot \frac{K_3}{\text{Pe}(m,s)} \text{ (5.22b)}
\]

\[
D = - \frac{3 \vartriangle \Phi_s}{\text{Pe}(m,s)} \text{ (5.22d)}
\]

\[
E = \frac{- y^2}{\text{Pe}(h,s)} + s + W_s \left\{ \frac{2}{\text{Pe}(h,s)} + \frac{3 \vartriangle \Phi_s}{\text{Pe}(h,s)} - \frac{3 \vartriangle \Phi_s}{\text{Pe}(m,s)} \cdot \frac{K_3}{\text{Pe}(h,s)} \right\} \text{ (5.22e)}
\]

43
\[ F = - \frac{3 \cdot \text{Bi}(h)}{\text{Pe}(h, s)} \]  

(5.22f)

\[ H = - \frac{3 \cdot \text{Bi}(h)}{\text{Pe}(h, s)} \cdot \Phi \mu \]  

(5.22h)

\[ I = s + y - \frac{y^2}{\text{Pe}(h, f)} + \frac{2}{\text{Pe}(h, f)} + \frac{3 \cdot \text{Bi}(h)}{\text{Pe}(h, s)} \cdot \Phi \mu \]  

(5.22i)

\[ R_1 = \frac{b_0}{\text{Pe}(m, a)} - \frac{1}{(y \cdot b_0 + b_1)} \]  

(5.22j)

\[ R_2 = - \frac{1}{\text{Pe}(h, s)} (y \cdot g_{s0} + g_{s1}) \]  

(5.22k)

\[ R_3 = \frac{g_{f0}}{\text{Pe}(h, f)} - \frac{1}{\text{Pe}(h, f)} (y \cdot g_{f0} + g_{f1}) \]  

(5.22l)

from the boundary conditions at the entrance of the reactor (eqns. (3.27), (3.34) and (3.37)) follows:

\[ \frac{\partial U_f}{\partial x} \bigg|_{x=0^+} = \text{Pe}(m, a) \left[ - \frac{U_f}{x=0^-} - \frac{U_f}{x=0^+} \right] \Rightarrow \]  

(5.23)

\[ b_1 = \text{Pe}(m, a) \cdot (b_0 - 1/s) \]

(5.24)

\[ g_{f1} = \text{Pe}(h, f) \cdot (g_{f0} - \Theta_{1n}/s) \]  

(5.25)

substitution of equations (5.23), (5.24) and (5.25) into (5.22j-1) gives for \( R_1 \), \( R_2 \) and \( R_3 \):

\[ R_1 = - \frac{y \cdot b_0}{\text{Pe}(m, a)} + \frac{1}{s} \]  

(5.26)
As a result of the Laplace transforms with respect to $\tau$ and $x$, the four partial differential equations are reduced to four linear equations of $U_t$, $U_s$, $\theta_t$ and $\theta_s$, from which $U_t$, $U_s$, $\theta_t$ and $\theta_s$ can easily be calculated, equations (5.9), (5.13), (5.17) and (5.21). So far the solution of the model equations is analytic.

5.2 Special cases

Adsorption equilibrium is not a function of temperature ($K_3=0$)

In this case element $B$ of the matrix in equation (5.22) is zero, and consequently the solution for $U_t$ (eqn. 5.29) becomes

$$\hat{U}_t = R_1/A$$  \hspace{1cm} (5.32)

The inverse Laplace transformation with respect to $x$ can easily be done analytically with the method of residues, which has been explained in paragraph 4.3.

The roots of the denominator $A$ (eqn. 5.22a) are

$$y_{1,2} = \frac{Pe(m,a)}{2} \pm \sqrt{\frac{Pe(m,a)^2}{4} + Pe(m,a).s + 3.m.\Phi_s \frac{Pe(m,a)}{Pe(m,s)}}$$

$$y_1 : + \quad y_2 : -$$  \hspace{1cm} (5.33)
Boundary condition (3.28) states that $U_f$, and so $\bar{U}_f$, tends to zero for $x$ to infinity. Because of the positive exponential in the numerator of residue 1, this residue has to be zero, so, for $\gamma_1$, $R_1$ has to be zero: (equation (5.26))

\[
1 - \frac{y_1 \cdot b_0}{\text{Pe}(m,a)} = 0 \implies b_0 = \frac{\text{Pe}(m,a)}{s \cdot y_1}
\]  
(5.34)

From the second residue follows:

\[
\frac{\text{Pe}(m,a)}{s \cdot y_1} U_f = \exp(x \cdot y_2) = b_0 \cdot \exp(x \cdot y_2)
\]  
(5.35)

Adsorption heat is zero ($\Gamma = 0$)

In this case element D of the matrix equation (5.22) is zero, and consequently the solutions for $\hat{\theta}_s$ and $\hat{\theta}_f$ (eqns. 5.30 and 5.31) become

\[
\hat{\theta}_s = -\frac{R_2 \cdot H + R_3 \cdot E}{E \cdot I - H \cdot F}
\]  
(5.36)

\[
\hat{\theta}_f = \frac{R_2 \cdot I - R_3 \cdot F}{E \cdot I - H \cdot F}
\]  
(5.37)

5.3 Inverse Laplace Transformation with Respect to Place

Equation (5.9) can directly be inverse transformed with the result:

\[
\bar{U}_s = \left[ \frac{K_3}{\bar{U}_f + \frac{K_3}{K_2}} \hat{\theta}_s \right] \frac{\sinh(\gamma(K_2 \cdot s \cdot \text{Pe}(m,s)))}{\gamma} \sinh(\gamma(\ldots) - \sinh(\gamma(\ldots)) + \sinh(\gamma(\ldots)) - \frac{K_3}{K_2} \hat{\theta}_s}
\]  
(5.38)

and so, after inverse transformation of $\hat{\theta}_f$ and $\hat{\theta}_s$, $\bar{U}_f$ can be calculated from these inverse transforms.

The inverse Laplace transformation of the equations (5.29), (5.30) and (5.31) can be done by the method of residues, described in paragraph 4.3. Therefore, we have to know the singularities of these functions, that is, the roots of the denominator polynomial. Each root leads to an exponential term.
of the inverse transform. In all these three equations the
denominator polynomial is given by \( A.(E.I - H.F) - B.D.I \). This
is a complex sixth degree polynomial for \( y \). It is important to
notice that this polynomial is a function of \( s \), because, as an
input for the Fast Fourier Transform, we need the inverse
transform with respect to \( x \) for a range of different \( s \) values.
Consequently, the inverse Laplace transform with respect to \( x \)
has to be calculated for each \( s \)-value. The roots of a complex
function can be calculated numerically, for example by using
Laguerre’s method (Press et al., 1987).

Three roots have a positive real part, leading to growing
exponentials for larger \( x \)-values, and three roots have a
negative real part, leading to decaying exponentials for larger
\( x \)-values. Because of the boundary conditions (3.28), (3.35) and
(3.38), that state that \( U_r, \Theta_r \) and \( \Theta_s \), and so \( U_r, \Theta_r \) and \( \Theta_s \),
tend to zero for \( x \) to infinity, the residues for the positive
roots have to be zero. This leads for each of the equations
(5.29), (5.30) and (5.31) to three equations:

\[
\begin{align*}
R_1 . (E.I - F.H) - R_2 . B.I + R_3 . B.F & = 0 \quad (5.39) \\
- R_1 . D.I + R_2 . A.I - R_3 . A.F & = 0 \quad (5.40) \\
R_1 . D.H - R_2 . A.H + R_3 . (A.E - B.D) & = 0 \quad (5.41)
\end{align*}
\]

Here, it becomes clear, why in paragraph 3.6.5 the boundary
conditions of a system with an open exit were chosen.

The parameters \( R_1, R_2 \) and \( R_3 \) are functions of the unknown
variables \( b_0, g_{r0} \) and \( g_{s0} \), which can now be calculated from
each of the sets of three equations (5.39), (5.40) and (5.41).
Each set must give the same results for \( b_0, g_{r0} \) and \( g_{s0} \).
However, if \( K_3 \) equals zero (\( B=0 \)), equation (5.39) can not be
used because in that case, \( R_2 \) and \( R_3 \) are eliminated. If \( \Gamma \)
equals zero (\( D=0 \)), equations (5.40) and (5.41) can not be used
because of elimination of \( R_1 \).

With these values of \( b_0, g_{r0} \) and \( g_{s0} \) the residues for the roots
with negative real parts can be calculated. The sum of these
three residues is the inverse Laplace transform.

In the special case that the adsorption equilibrium is not a
function of temperature (\( K_3=0 \)), the singularities can be
calculated analytically (equation 5.3). The inverse
Laplace transform is given by the equations (5.34) and (5.35).

For the special case that the adsorption heat is zero (\( \Gamma=0 \)),
equations (5.30) and (5.31) can be simplified to (5.36) and
(5.37). The singularities then can be found by calculating the
four roots of \( E.I - H.F \). The boundary conditions \( g_{s0} \) and \( g_{r0} \)
can be calculated from one of the numerators of the equations
(5.36) and (5.37) and the roots with positive real parts:
\[-R_2 \cdot H + R_3 \cdot E \quad \text{positive roots} = 0 \quad (5.42)\]
\[R_2 \cdot I - R_3 \cdot F \quad \text{positive roots} = 0 \quad (5.43)\]

In paragraph 4.5 has been explained that if a function has a singularity at the origin, this singularity can be eliminated by subtracting \( f(\omega)/s \) from the Laplace function (equation (4.29)). \( f(\omega) \) is the first Laplace domain function, multiplied by \( s \), for \( s \) to zero (equation (4.27)). This can be calculated by inverse transformation of the second Laplace domain function, multiplied by \( s \), for \( s \) equal to zero. Multiplication of the functions by \( s \) can be done by multiplying \( R_1 \), \( R_2 \) and \( R_3 \) by \( s \). When \( s \) is equal to zero, it follows from (5.26), (5.27) and (5.28) that:

\[s \cdot R_1 \quad \text{at } s=0 = 1 \quad (5.44)\]
\[s \cdot R_2 \quad \text{at } s=0 = 0 \quad (5.45)\]
\[s \cdot R_2 \quad \text{at } s=0 = \Theta_{1a} \quad (5.46)\]

If \( s \) equals zero, \( \Phi_a \) becomes zero, and thus \( B \) and \( D \) (equation (5.22)) are zero. Multiplication of equations (5.29), (5.30) and (5.31) by \( s \) and substitution of equations (5.44), (5.45) and (5.46) then gives:

\[s \cdot \tilde{U}\tau = \frac{1}{A} \quad (5.47)\]
\[s \cdot \tilde{\Theta}_s = -\frac{F \cdot \Theta_{1a}}{E \cdot I - H \cdot F} \quad (5.48)\]
\[s \cdot \tilde{\Theta}_\tau = \frac{E \cdot \Theta_{1a}}{E \cdot I - H \cdot F} \quad (5.49)\]

Equation (5.47) can be inverse transformed analytical. From equation (5.33) follows that for \( s \) equal to zero, the roots of (5.47) are \( Pe(m,a) \) and zero. Substitution into (5.35), multiplied by \( s \) shows that \( s \cdot \tilde{U}_\tau \) for \( s \) to zero, and thus \( U_\tau \) for \( \tau \) to infinity, is equal to one in all cases. From (5.9) follows that for \( s \) to zero, \( U_s \) becomes equal to \( U_\tau \) in all cases. This is of course correct, because in the stationary situation, all concentrations in the bed will be equal to the concentration of the inlet, which is one in dimensionless form.

The inverse Laplace transform of the equations (5.48) and (5.49) must be calculated by the method previously described in this paragraph.
5.4 Inverse Laplace Transformation with Respect to time

In paragraph 4.5, the theory of the inverse Laplace transformation by applying the Fast Fourier Transform has been discussed. As input for the Fast Fourier Transform we need the function in the s,x-domain at the s-values \( s = a + ink/T \), for \( k \) from 0 to a power of 2, with \( T \) half of the time interval for which the time function is calculated. In paragraph 4.5 has been discussed in what range the \( a \)-value must be, and how this choice can be simplified. Essentially, for the number of points \( N \), all powers of two can be chosen. However, for a small number of points, for example 32, the result will be less accurate than for a large number of points, for example 512. A compromise has to be made between a fast inaccurate result and a more accurate result which will take more time. The only limit to the number of points is the memory size of the computer.

As explained in paragraph 4.5, the real part of the function is even \( (\text{Re}\{ F(s) \} = \text{Re}\{ F(-s) \} ) \), and the imaginary part is odd \( (\text{Im}\{ F(s) \} = -\text{Im}\{ F(-s) \} ) \). In addition, the function is periodic over \( \omega \) with a period \( nN/T \). This means that the real part of the function for \( k = N/2 + 1 \) to \( K = N \) can be calculated from the part for \( k = 0 \) to \( N/2 \) by folding about the point at \( k = N/2 \). For the imaginary part, after folding, the sign of the function for \( k = N/2 + 1 \) to \( N \) has to be changed. The two arrays calculated now can be used as input for the Fast Fourier Transform. The Fast Fourier Transform gives as a result two arrays; one is the real time function and one is the imaginary time function, which will be zero. As explained in paragraph 4.5, the result of the Fast Fourier Transform has to be multiplied by \( \exp(2ajT/N) \), for those cases were the \( a \)-value unequals zero, with \( j \) the point index in the time array.
CHAPTER 6

THE COMPUTER PROGRAM

6.1 Program Structure

In the previous chapter, the model equations were Laplace transformed, both with respect to time and place. The set of equations in the second Laplace domain could easily be solved. So far the solution is analytical. The inverse Laplace transformations have been calculated numerically. In paragraph 5.3 and 5.4 has been described how this can be done.

In paragraph 4.5 has been explained that the a-value of the complex line-integration of the inverse Laplace transformation (eqn. 4.7) can always be chosen zero, because the singularity at the origin can be eliminated by subtracting f(∞)/s from the first Laplace domain function (eqn. (4.29)). However, after this elimination the function can not easily be calculated for s equal to zero and so, the a-value must still be chosen. This will be discussed more extensively in paragraph 6.3.

In paragraph 4.6 is an efficient use of the Fourier Transform described. By rearrangement of the elements, half of the memory size can be saved. In order to keep clarity, this method is not used in the computer program.

The program can be divided into three parts. The main program performs the input, Fast Fourier Transform and the output. The procedure FirstInverseLaplaceTransform calculates for a specified s-value the first inverse Laplace transform of the functions (5.9), (5.29), (5.30) and (5.31). The procedure FirstInverseLaplaceTransformForSIsZero calculates the value of the first inverse Laplace transform for the functions in the second Laplace domain multiplied by s for s equal to zero. This stationary value is used to eliminate the singularity in the origin (paragraph 4.5).

The present program has been developed in Turbo Pascal 4.0 on a Personal Computer with 8086 processor and 8087 mathematical coprocessor. The Turbo Pascal Numerical Methods Toolbox and the Turbo Pascal Graphix Toolbox have been used.

In the appendices A, B and C, for each part of the program a diagram is given of the procedures used by that part. The procedures are also listed with for each procedure, its function, heading and local variables.
6.2 Guidelines for the Input

As input for the program are required:

1 - The number of points you want to use for the Fast Fourier Transform.
2 - The number of points you want to use for tapering Im(F(s)).
3 - x, the axial place in the reactor where you want to know the breakthrough curves.
4 - n, the radial place in the particle where you want to know the 'breakthrough curves'.
5 - The time interval for which you want to calculate the inversed function. The interval will always start at t=0, and must be chosen such that the breakthrough curves have almost reached their stationary values for t->∞.
6 - The time interval for which you want to see a plot. This can be chosen because, sometimes, the time-function is for high τ-values strongly oscillating, while the function is smooth for low τ-values.
7 - The value of a.
8 - Whether you want to differentiate F(s) or not.
9 - In the case you differentiate F(s), whether you want to integrate f(t) or not.
10 - The process parameters Pe(m,s), Pe(m,a), Φ, Bi(m), μ, Pe(h,f), Pe(h,s), Bi(h), Γ, W, Ws, K1, K2, K3 and Θ18.

For a specified problem the x and n values will be given, as well as the process parameters Pe(m,s), Pe(m,a), Φ, Bi(m), μ, Pe(h,f), Pe(h,s), Bi(h), Γ, W, Ws, K1, K2, K3 and Θ18. The other input variables must be found, basically by trial and error.

For the first runs, the number of points can better be chosen small, for example 64, because more points will take more time, while the accuracy is not needed yet. The number of points for tapering Im(F(s)) can always be chosen equal to the number of points minus 2. For a small number of points the discontinuity of imaginary part will be rather large. Therefore, in that case tapering is important for the suppression of oscillations. Because of this strong tapering the result will also be less accurate. When the correct input parameters are found, more points can be used, in which case tapering is less important.

The time interval has to be chosen such that the breakthrough curves have almost reached their stationary values for t->∞. Consequently, it can better be chosen too large than too small.

When it is uncertain whether differentiation of F(s) will give correct results or not, differentiation can best be tried, because in that case the a-value can be chosen zero. If differentiation of F(s) does not give correct results, an a-value of 1/2T, with 2T the time interval for which the transform is calculated, usually will do. This will be discussed in paragraph 6.5.
<table>
<thead>
<tr>
<th>Case</th>
<th>$K_3$</th>
<th>$\Gamma$</th>
<th>Concentration</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>Equal to Chen and Hsu for large $Pe(m,a)$</td>
<td>For small $\Gamma$ equal to case 3</td>
</tr>
<tr>
<td>2</td>
<td>$\neq0$</td>
<td>0</td>
<td>For small $K_3$ equal to case 1</td>
<td>For small $\Gamma$ equal to case 4</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>$\neq0$</td>
<td>Equal to Chen and Hsu for large $Pe(m,a)$</td>
<td>Same method as concentration cases 2 and 4</td>
</tr>
<tr>
<td>4</td>
<td>$\neq0$</td>
<td>$\neq0$</td>
<td>For small $K_3$ equal to case 3</td>
<td>Same method as concentration cases 2 and 4</td>
</tr>
</tbody>
</table>
6.3 Testing the Program

When $K_3$ equals zero, the concentration breakthrough curves can be compared with those of Chen and Hsu (1987). Chen and Hsu however, assume an other boundary condition at the entrance of the reactor (see paragraph 3.6.5). For a small axial diffusion coefficient (large $Pe(m,a)$), these boundary conditions become identical, and calculation of our model for large $Pe(m,a)$-values must give the same result as Chen and Hsu's model with the same process parameters.

When $K_3$ is zero, the inverse Laplace transform of the fluid concentration with respect to place can be calculated analytical (equation (5.35)). When $K_3$ is not equal to zero, the inverse Laplace transform with respect to place is calculated from equation (5.29) by the method of residues, completely different from equation (5.35). The general method for $K_3$ unequal to zero can be verified by taking a very small $K_3$-value. The concentration breakthrough curve then must be almost identical to the curves for $K_3=0$.

When $\Gamma$ is not equal to zero, the temperature breakthrough curves are calculated by the same procedure as the fluid concentration breakthrough curve when $K_3$ is not equal to zero. Therefore, these temperature breakthrough curves can be expected to be correctly calculated.

When $\Gamma$ is equal to zero, the inverse Laplace transform with respect to place is calculated from equations (5.36) and (5.37), instead of (5.30) and (5.31). For a small $\Gamma$-value the results must be almost identical to the results for $\Gamma=0$.

Using the methods described above, the breakthrough curves for all possible combinations of $K_3$ and $\Gamma$-values can be verified, starting with comparison with the results of Chen and Hsu. This is summarized in table 6.1. All methods for testing the program have been used, and no differences were found with what was expected.

The stationary values of the breakthrough curves can also be used as verification. The stationary values of the concentration curves must be equal to one, and the stationary values of the temperature curves must be equal to the values calculated by the procedure FirstInverseLaplaceTransformForSIsZero.

Another verification method is a parameter sensitivity test. A small change of any of the process parameter $Pe(m,s)$, $Pe(m,a)$, $\Phi$, $Bi(m)$, $\mu$, $Pe(h,\varepsilon)$, $Pe(h,s)$, $Bi(h)$, $\Gamma$, $W_r$, $W_s$, $K_1$, $K_2$, $K_3$ and $\Theta_m$ must give a small change of the calculated breakthrough curves. This indeed is the case.
6.4 Accuracy

During the testing of the program some important causes for inaccuracies were found. These will be described in paragraph 6.5.

Application of the Fast Fourier Transform is an intrinsic cause of inaccuracies. Especially when a small number of points is used, the result will not be very accurate. When doubling of the number of points does not change the calculated curves anymore, the inaccuracies caused by the fast Fourier Transform are negligible.

Except for those cases where very large or very small process parameters are used, the inaccuracies of the process parameters can be expected to be more important than the inaccuracies of the calculations. Inaccuracies of measured breakthrough curves can be expected to be more important too.

6.5 Numerical Problems

The choice of a

In paragraph 4.5 has been explained that the choice of the a-value can be avoided by subtracting \( f(\omega)/s \) from \( F(s) \), which eliminates the singularity of \( F(s) \) at the origin (eqn. (4.29)). One difficulty in this method is that \( F(s)-f(\omega)/s \) can not easily be calculated for \( s=0 \) if \( F(s) \) has a singularity at the origin. Therefore, if \( F(s) \) can not be differentiated, the a-value has still to be chosen.

If the a-value is chosen too high, the growing exponential \( \exp(\alpha t) \) (see paragraph 4.5) will intensify inaccuracies. On the other hand, when the a-value is chosen very close to zero, the solution is not influenced by the singularity at the origin anymore, because then this is eliminated. So, the only restriction for choosing a small a-value is the range of variables and the accuracy of the computer. An a-value of \( 1/2T \) appeared to be a satisfying initial value.

Finding the singularities

The singularities of the function in the second Laplace domain are equal to the roots of the denominator polynomial. These are found by the Laguerre method (Press et al., 1987), though sometimes the result is inaccurate. This problem can be solved by scaling the polynomial. The coefficients of \( y \) appeared to be on the order of \( 10^{-21} \), and so, substitution of \( y/100 \) for \( y \) gives a polynomial with coefficients of the same order of magnitude.
Concentrations $U_f(T)$ and $U_s(T)$

Temperatures $\Theta_f(T)$ and $\Theta_s(T)$

**Concentration $Q(T)$**

**Process Parameters:**

- $P_e(s, a) = 0.2$
- $P_e(s, b) = 500.0$
- $E_i(s) = 10000.0$
- $F_i(s) = 20000.0$
- $P_e(s, h) = 600000.0$
- $S_i(h) = 100000.0$

**Fixed-Bed Breakthrough Curves of $U_f(T)$, $U_s(T)$, $\Theta_f(T)$ and $Q(T)$**

**Time Period:** 4000.00 s

**Number of points:** 256

- $x = 1.000000$
- $a = 0.000000$
- $\eta_f = 0.000000$
- $\phi_i = 1.000000$

**f(s) are differentiated**

**f(t) are integrated**

**Computer Time:** 115.80 sec

**Figure 7.1 Combined wave: $K_2 < \phi, K_3 = 0$**

**Concentration $Q(T)$**

**Process Parameters:**

- $P_e(m, s) = 0.2$
- $P_e(m, a) = 500.0$
- $E_i(m) = 10000.0$
- $F_i(m) = 20000.0$
- $P_e(h, m) = 600000.0$
- $S_i(h) = 100000.0$

**Fixed-Bed Breakthrough Curves of $U_f(T)$, $U_s(T)$, $\Theta_f(T)$ and $Q(T)$**

**Time Period:** 4000.00 s

**Number of points:** 256

- $x = 1.000000$
- $a = 0.000000$
- $\eta_i = 0.000000$
- $\phi_i = 1.000000$

**f(s) are differentiated**

**f(t) are integrated**

**Computer Time:** 113.30 sec

**Figure 7.2 Intermediate regime: $K_2 = \phi, K_3 = 0$**
CHAPTER 7

RESULTS

7.1 Prediction of breakthrough regimes by the model

The two breakthrough regimes, pure thermal wave and combined wave, described in chapter 2.4, are predicted by the model and computer calculations. Starting point for the model predictions is equation (2.13). Equation (2.13) is a sufficient condition for the existence of a combined wave front, and can be written in dimensionless form as follows:

\[ \Phi > \frac{Q_2 - Q_1}{U_{f2} - U_{f1}} \]  \hspace{2cm} (7.1)

In those cases where both \( K_1 \) and \( K_2 \) are zero, \( (Q_2 - Q_1)/(U_{f2} - U_{f1}) \) is equal to \( K_2 \). In figures (7.1), (7.2) and (7.3) breakthrough curves are given for \( K_2 \)-values smaller than, equal to and greater than \( \Phi \), respectively. In order to get breakthrough curves with clear plateaus, the heat transfer resistance of the film must be small (large \( Bi(h) \)).

Equations (2.8) and (2.9) can be written in dimensionless form as follows:

\[ \frac{\Theta_1 - \Theta_2}{\Gamma} = \frac{1}{1/\Phi - 1} \frac{1}{U_{f2} - U_{f1}} \frac{Q_2 - Q_1}{Q_1 - Q_2} \]  \hspace{2cm} (7.2)

\[ \frac{\Theta_2 - \Theta_3}{\Gamma} = \frac{1}{1/\Phi - 1} \frac{1}{U_{f3} - U_{f2}} \frac{Q_3 - Q_2}{Q_2 - Q_1} \]  \hspace{2cm} (7.3)

As predicted by equation (7.1), there is a combined wave breakthrough regime for \( K_2 \) smaller than \( \Phi \) (figure (7.1)). The temperature plateau is in accordance with equation (7.2). For \( K_2 \) larger than \( \Phi \), a pure thermal wave regime appears. This in accordance with equations (2.14) and (2.15). In this case, the temperature step is the maximum temperature that can be reached, described by equations (7.3) and (2.16). For \( K_2 \) equal to \( \Phi \), an intermediate regime is formed.

In figures (7.4), (7.5) and (7.6) three cases are shown with \( K_2 \) smaller than zero. In all those cases a combined wave regime appears. The temperature plateaus are described by equations (7.2) and (7.3).
Concentrations $U_f(r)$ and $U_s(r)$

Temperatures $\theta_f(r)$ and $\theta_s(r)$

Concentration $Q(r)$

Fixed-Bed Breakthrough Curves of $U_f(r)$, $\theta_f(r)$, $U_s(r)$, $\theta_s(r)$ and $Q(r)$

Time Period = 2000.00 (−)
Number of points = 256
$x = 1.00000$
$a = 0.00000$
$\eta = 0.00000$
f($s$) are differentiated
f($t$) are integrated

Computer Time = 112.50 sec

Figure 7.3 Thermal wave: $K_2 > \Phi$, $K_3 = 0$

Concentrations $U_f(r)$ and $U_s(r)$

Temperatures $\theta_f(r)$ and $\theta_s(r)$

Concentration $Q(r)$

Fixed-Bed Breakthrough Curves of $U_f(r)$, $\theta_f(r)$, $U_s(r)$, $\theta_s(r)$ and $Q(r)$

Time Period = 4000.00 (−)
Number of points = 256
$x = 1.00000$
$a = 0.00000$
$\eta = 0.00000$
f($s$) are differentiated
f($t$) are integrated

Computer Time = 127.00 sec

Figure 7.4 Combined wave: $K_2 < \Phi$, $K_3 < 0$
Figure 7.5 Combined wave: $K_2 = \Phi$, $K_3 < 0$

Figure 7.6 Combined wave: $K_2 > \Phi$, $K_3 < 0$
Concentrations \( U_f(t) \) and \( U_s(t) \)

Temperatures \( \theta_f(t) \) and \( \theta_s(t) \)

Concentration \( Q(t) \)

Fixed-Bed Breakthrough Curves of \( U_f(t), \theta_f(t), U_s(t), \theta_s(t) \) and \( Q(t) \)

Time Period = 60000.00 (-)
Number of points = 1024
\( x = 1.000000 \)
\( a = 0.000001 \)
\( \text{eta} = 0.000000 \)

Computer Time = 586.78 sec

**Process Parameters:**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pe}(m.s) )</td>
<td>5.0</td>
</tr>
<tr>
<td>( \text{Pe}(m.a) )</td>
<td>500.0</td>
</tr>
<tr>
<td>( \text{Bi}(m) )</td>
<td>10000.0</td>
</tr>
<tr>
<td>( \mu )</td>
<td>1.5</td>
</tr>
<tr>
<td>( \text{Pe}(h.f) )</td>
<td>20000.0</td>
</tr>
<tr>
<td>( \text{Pe}(h.s) )</td>
<td>60000.0</td>
</tr>
<tr>
<td>( \Phi )</td>
<td>1000.0</td>
</tr>
<tr>
<td>( \text{Bi}(h) )</td>
<td>50.0</td>
</tr>
</tbody>
</table>

**Figure 7.7** Example breakthrough curves
From the good description of both the regimes and the temperature plateaus can be concluded that the model is a satisfying description of the adsorption process. The linearised isotherm appears to be no restriction for the prediction of breakthrough regimes.

7.2 Example of the Program Output

In figure 7.7, an example is given of the program output. The process parameters are chosen such that all the processes included in the model are demonstrated. In Appendix D, a comparison of execution time and accuracy for the breakthrough curves with varying number of sample points is given.

7.3 Description of Experimental Breakthrough Curves

A simplified version of the model has been used to describe concentration breakthrough curves of a real fixed-bed reactor.

At the laboratory for Chemical Technology, the removal of SO$_2$ from gas streams is studied. This removal can be done by the reaction of SO$_2$ with CaO in a fixed-bed reactor. The CaO is deposited on porous alumina particles. The following reaction takes place:

$$\text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{CaO}/\alpha-\text{Al}_2\text{O}_3 \rightarrow \text{CaSO}_4/\alpha-\text{Al}_2\text{O}_3$$ (7.4)

Possibly, SO$_3$ acts as an intermediate component. Concentration breakthrough curves are measured for varying flow rates. Because the measured temperature changes can be neglected, a simple version of the computer program could be used. Some process data and an overview of the experiments are given in tables 7.1 and 7.2. The diffusion coefficients of table 7.1 are calculated from equations given by Perry (1985).

As input parameters for the program are needed, $Pe(m,s)$, $Pe(m,a)$, $u$, $Bi(m)$ and $K_2$. The Biot number is chosen large, because the film diffusion will not be important. $K_2$ can be calculated from the amount of CaO initially present in the reactor, because when the fluid concentration has reached its stationary value, all CaO must have been reacted.

Breakthrough curves calculated with the parameters of tables 7.1 and 7.2 differ significantly from the experimental curves. Therefore, the experimental curves are tried to be fitted by varying the process parameters. The bed porosity can be expected to be measured correctly, and the axial diffusion and film resistance do not influence the result significantly. Therefore, only $Pe(m,s)$ and $K_2$ are varied. The fit is done manually and is not the best possible.

Results are given in figures 7.8-7.12. From these figures can
### Table 7.1 Process parameters of SO₂ removal
**Diffusion coefficients from Perry (1985)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed length</td>
<td>L = 4.9E-2 (m)</td>
</tr>
<tr>
<td>Particle Radius</td>
<td>Rₚ = 1.34E-3 (m)</td>
</tr>
<tr>
<td>Bed Porosity</td>
<td>ε = 0.37 (-)</td>
</tr>
<tr>
<td>μ (1-ε)/ε</td>
<td>1.7 (-)</td>
</tr>
<tr>
<td>Axial Diffusion Coefficient</td>
<td>Dₐ = 1.34E-4 (m²/s)</td>
</tr>
<tr>
<td>Pore Diffusion Coefficient</td>
<td>Dₚ = 1.833E-7 (m²/s)</td>
</tr>
<tr>
<td>Film resistance</td>
<td>Bi(m) = 10000 (m/s)</td>
</tr>
<tr>
<td>Maximum Loading</td>
<td>K₂ = 9.13E+4 (-)</td>
</tr>
</tbody>
</table>

### Table 7.2 SO₂ removal experiments

<table>
<thead>
<tr>
<th>Run</th>
<th>120</th>
<th>115</th>
<th>114</th>
<th>121</th>
<th>112</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sup. flow vel. (m/s)</td>
<td>0.12</td>
<td>0.15</td>
<td>0.20</td>
<td>0.30</td>
<td>0.50</td>
</tr>
<tr>
<td>Flow velocity (m/s)</td>
<td>0.324</td>
<td>0.405</td>
<td>0.541</td>
<td>0.881</td>
<td>1.351</td>
</tr>
<tr>
<td>Pe(m,s) (-)</td>
<td>65</td>
<td>81</td>
<td>108</td>
<td>162</td>
<td>270</td>
</tr>
<tr>
<td>Pe(m,a) (-)</td>
<td>120</td>
<td>150</td>
<td>200</td>
<td>300</td>
<td>500</td>
</tr>
</tbody>
</table>
Experimental and Model Curves

Figure 7.8 Modelling of experiment nr 120

Figure 7.9 Modelling of experiment nr 115
Figure 7.10 Modelling of experiment nr 114

Figure 7.11 Modelling of experiment nr 121
be seen that a reasonably good description of the experimental curves is obtained by $\text{Pe}(\text{m},s)$ and $K_2$-values that are smaller than those of tables 7.1 and 7.2. Especially the Peclet numbers are smaller.

A few causes can be given for the deviations of the model curves:

* For the calculation of the pore diffusion coefficient, the average pore diameter and the tortuosity factor are required. It is difficult to determine these parameters accurate.

* It could be possible, that not all the CaO deposited on the alumina is available for the reaction. Maybe a part of it is enclosed by the alumina. Then, the maximum loading, $K_2$ is smaller than expected.

* For the description of the reaction, an equilibrium, represented by a linear isotherm, had to be assumed. Possibly, this is a too simplified description of the reaction.

* The mechanism of the reaction is not fully understood yet. Especially the role of $\text{SO}_3$ is not clear. Also a variety of reaction products of CaO and $\text{Al}_2\text{O}_3$ can be important.

### 7.4 Execution Time

The speed of the program could not be compared with other methods, because no other methods were available. Chen and Hsu (1987) however, compared their program for isothermal adsorption processes with earlier methods. The FFT method was almost three orders of magnitude faster than the collocation method of Raghavan and Ruthven (1983) and more than four orders of magnitude faster than an analytic solution of Rasmuson and Neretnieks (1980). Therefore, it can be expected that the present method is several orders of magnitude faster than other methods.

The present program takes 8.2 seconds for the problem of Chen and Hsu (1987), that they solve in 0.038 seconds (128 sample points). After extension with temperature breakthrough curves, calculation takes 66.4 seconds. With this, the calculation of these problems have been brought to the level of Personal Computers, while the method as such can be applied to the much larger problem of parameter estimation.
Figure 7.12 Modelling of experiment nr 112
The purpose of this study was to develop a model and a computer program for the description of non-isothermal fixed-bed processes. This is partially succeeded. A model has been developed for a non-isothermal fixed-bed adsorption process. The program is very fast, but has two important restrictions: there are no radial gradients of concentrations and temperatures included in the model, and the adsorption isotherm has to be a linear function of concentration and temperature. The model can also be used for gas-solid reactions if the reaction equilibrium can be described by a linear function of the reactant concentration and temperature.

It has been shown that the Fast Fourier Transform can be used for the solution of the model equations of a non-isothermal fixed-bed reactor. For the application of the Fast Fourier Transform, the model equations had to be Laplace transformed with respect to time and place. For both inverse Laplace transforms, numerical problems had to be solved. The resulting computer program calculates concentration and temperature breakthrough curves in a few minutes on a Personal Computer with 8086 processor and 8087 mathematical coprocessor. Although a comparison with other methods of solution could not be made, because no other methods were available, the present method can be expected to be several orders of magnitude faster than other methods.

Solving differential equations by applying the Fast Fourier Transform, appears to be a very fast method. However, it can only be applied for linear function of concentration and temperature. This is especially a restriction for adsorption equilibria and reaction kinetics, which are generally described by non-linear equations. For example application for a second order chemical reaction is not possible. These equations must be linearised in order to apply the Fast Fourier Transform. A compromise has to be made between this fast method, that can only be used for linearised equations, and much slower methods for which this simplification is not necessary.

Although a simplified isotherm had to be assumed, the model describes quantitative the existence of different breakthrough regimes and temperature plateaus. The effects of variations of the process parameters, such as diffusion coefficients and heat transfer resistances are described qualitative. Comparison with the results of a program that solves the model equations by a different method, can be advised.

In order to make the program useful for a more general set of fixed-bed processes, future developments should be directed towards a more general adsorption isotherm and the radial components of the model equations. Especially the possibility of non-linear isotherms would make the program very powerful.
ACKNOWLEDGMENT

This study would not have been possible without the support of Albert Gerritsen and Peter Verheijen. It has been a pleasant and fruitful co-operation.
NOTATION

$C_f$  fluid concentration  mole/m³
$C_a$  concentration of the fluid in the pores  mole/m³
$C_o$  concentration of the incoming fluid  mole/m³
$C_{pf}$  heat capacity of the fluid  J/kg/K
$C_{ps}$  heat capacity of the solid  J/kg/K
$d_P$  particle diameter  m
$D_a$  axial mass dispersion coefficient of the fluid  m²/s
$D_p$  diffusion coefficient in the pores  m²/s
$D_r$  radial mass dispersion coefficient of the fluid  m²/s
$h_f$  film heat transfer coefficient  J/m²/s/K
$h_{wf}$  heat transfer coefficient from fluid to wall  J/m²/s/K
$h_{ws}$  heat transfer coefficient from solid to wall  J/m²/s/K
$-\Delta H$  adsorption heat  J/mole
$k_f$  film mass transfer coefficient  m/s
$L$  reactor length  m
$q$  adsorbed concentration  mole/m³
$r$  radial place in the reactor  m
$R$  reactor radius  m
$r_P$  radial place in the particle  m
$R_p$  particle radius  m
$t$  time  s
$T_f$  temperature of the fluid  K
$T_{in}$  temperature of the incoming fluid  K
$T_s$  temperature of the solid  K
$T_w$  temperature of the wall  K
$v$  intrinsic fluid velocity  m/s
$\Delta V$  volume over which balances are calculated  m³
$z$  axial place in the reactor  m

greek symbols:

$\varepsilon$  porosity of the bed  
$\Phi_f$  fluid flowrate  m³/s
$\lambda_f$  axial heat dispersion coefficient of fluid  J/m/s/K
$\lambda_r$  radial heat dispersion coefficient of fluid  J/m/s/K
$\lambda_s$  axial heat conduction coefficient of solid  J/m/s/K
$\lambda_r$  radial heat conduction coefficient of solid  J/m/s/K
$\rho_f$  fluid density  kg/m³
$\rho_s$  solid density per m³ particles  kg/m³
dimensionless parameters (paragraph 3.6.6):

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Bi$</td>
<td>Biot number, ratio of internal and external mass and heat transfer, $m =$ mass, $h =$ heat</td>
</tr>
<tr>
<td>$Pe$</td>
<td>Péclet number, ratio of transport by convection and transport by diffusion or conduction, $m =$ mass, $h =$ heat $f =$ fluid, $s =$ solid $a =$ axial, $r =$ radial</td>
</tr>
<tr>
<td>$Q$</td>
<td>adsorbed concentration</td>
</tr>
<tr>
<td>$U_f$</td>
<td>fluid concentration</td>
</tr>
<tr>
<td>$U_s$</td>
<td>fluid concentration in the pores</td>
</tr>
<tr>
<td>$W$</td>
<td>Wall heat transfer parameter, $f =$ fluid, $s =$ solid</td>
</tr>
<tr>
<td>$x$</td>
<td>axial place in the reactor</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>reactor length divided by reactor radius</td>
</tr>
<tr>
<td>$\beta$</td>
<td>reactor radius divided by particle radius</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>adiabatic temperature change divided by wall temperature</td>
</tr>
<tr>
<td>$\eta$</td>
<td>radial place in a particle</td>
</tr>
<tr>
<td>$\mu$</td>
<td>solid volume divided by fluid volume</td>
</tr>
<tr>
<td>$\Theta_f$</td>
<td>temperature of the fluid</td>
</tr>
<tr>
<td>$\Theta_s$</td>
<td>temperature of the solid</td>
</tr>
<tr>
<td>$\Theta_{in}$</td>
<td>temperature of the incoming fluid</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>radial place in the reactor</td>
</tr>
<tr>
<td>$\tau$</td>
<td>time</td>
</tr>
<tr>
<td>$\phi$</td>
<td>ratio of specific heats, solid/fluid</td>
</tr>
</tbody>
</table>
LITERATURE


61
Rasmussen, A.; Neretnieks, I.; Exact Solution of a Model for Diffusion in Particles and Longitudinal Dispersion in Packed Beds, AIChE Journal 26 (1980) 686

APPENDIX A  Diagram and List of the Procedures used by the Main Program

Program FixedBedBreakthroughCurves

GetSeconds A

DefaultConstants B

Initialize C

InputFFTParameters D

Function TestForPowersOfTwo: boolean E

MakeData F

InputProcesParameters G

FirstInverseLaplaceTransformForSIsZero H
Unit FILTNull

FirstInverseLaplaceTransform I
Unit FILT

ComplexFFT J
Unit FFTP2

CalculateSolid K

GraphicOutput L
uses Turbo Pascal Graphix Toolbox

SetPlot M

Integrate N

DiskOutput O
Program LaplaceInverse

Include file:
  Float.inc : Determines the setting of the SN compiler directive

Uses the Units:
  Dos, Crt : Turbo Pascal Unit
  Printer : Turbo Pascal Unit
  Complex : Complex calculations
  Initial : Input procedures
  Laguer : Laguerre's method for calculation of the roots of a complex polynomial
  Common : I/O routines for Numerical Toolbox
  GDriver : Turbo Pascal Graphix Toolbox
  GKernel : Turbo Pascal Graphix Toolbox
  GWindow : Turbo Pascal Graphix Toolbox
  GShell : Turbo Pascal Graphix Toolbox
  FILT : First Inverse Laplace Transform
  FILTNul : First Inverse Laplace Transform for s is zero
  FFTB2 : Turbo Pascal Numerical Methods Toolbox unit for Fast Fourier Transform

Types
  : Type declarations

Constants:
  IOerr : boolean = false  Flags an I/O error
  PrinterMode = 6

Global variables:
  NumPoints : Integer  Number of points for FFT
  NumPlot : Integer  Number of points for plot
  Numsmooth : Integer  Number of points for smoothing Im(F(s))
  k,i : Integer  Counters
  FConcReal : TNvectorPtr  Real part of U_f
  FConcImag : TNvectorPtr  Imaginary part of U_f
  FTempReal : TNvectorPtr  Real part of Θ_f
  FTempImag : TNvectorPtr  Imaginary part of Θ_f
  SConcReal : TNvectorPtr  Real part of U_s
  SConcImag : TNvectorPtr  Imaginary part of U_s
  STempReal : TNvectorPtr  Real part of Θ_s
  STempImag : TNvectorPtr  Imaginary part of Θ_s
  SolidReal : TNvectorPtr  Real part of Q
  SolidImag : TNvectorPtr  Imaginary part of Q
  FConcNul : TNcomplex  Stationary part of U_f
  FTempNul : TNcomplex  Stationary part of Θ_f
  SConcNul : TNcomplex  Stationary part of U_s
  STempNul : TNcomplex  Stationary part of Θ_s
  SolidNul : TNcomplex  Stationary part of Q
  Inverse : Boolean  True for inverse FFT
  Error : Byte  Flags if something went wrong
  a, omega : Float  Re(s) and Im(s)
  Ti : Float  Time interval considered
  Tp : Float  Time interval for plot
  StartSeconds : Real  Time before calculations
  EndSeconds : Real  Time after calculations
  Ch : Char  Help character

A-2
dif Char 'J' for differentiation of F(s)
int Char 'J' for integration of f(t)
x Float Axial distance in reactor
eta Float Radial distance in particle
PeMS, PeMA, Fi Float Pe(m, s), Pe(m, a), φ
BiM, BiH, Mu Float Bi(m), Bi(h), μ
PeHF, PeHS, Gamma Float Pe(h, f), Pe(h, s), Γ
Wf, Ws, Kl, K2, K3 Float Wf, Ws, K1, K2, K3
ThetaIn Float θ₁₈

A Procedure GetSeconds

Function: Read system time

Heading:
Out RealSeconds Real

Local Variables:
Hours Word
Minutes Word
Seconds Word
Hundredths Word

B Procedure DefaultConstants

Function: Initial values for process parameters

C Procedure Initialize

Function: Initialization of pointer array's

Heading:
Out FConcReal, FConcImag, FTempReal, FTempImag, SConcReal,
SConcImag, STempReal, STempImag, SolidReal, SolidImag, Error

D Procedure InputFFTParameters

Function: Input of Numpoints, Numsmooth, x, eta, Ti, Tp, a, dif
and int

Heading:
Out Numpoints, Numsmooth, x, eta, Ti, Tp, a, dif, int

E Function TestForPowersOfTwo: boolean

Function: Test Numpoints for power of two

Heading:
In NumPoints Integer

A-3
types:
ShortArray = array[1..13] of Integer

costants:
PowersOfTwo : ShortArray = (2, 4, 8, 16, 32, 64, 128, 256, 512, 1024, 2048, 4096, 8192)

Local variables:
  Term Integer
  Test Boolean

F Procedure MakeData

Function: calculation of the input array’s for FFT

Heading:
In  Numpoints, Ti, a, x, eta
Out FConcReal, FConcImag, FTempReal, FTempImag,
    SConcReal, SConcImag, STempReal, STempImag,
    FConcNul, FTempNul, SConcNul, STempNul

Local Variables:
  cosine Float  used for smoothing
  FiltFConc TNcomplex U_r(s,x)
  FiltFTemp TNcomplex Θ_r(s,x)
  FiltSConc TNcomplex U_s(s,x)
  FiltSTemp TNcomplex Θ_s(s,x)
  FConcHulp TNcomplex Help variables
  FTempHulp TNcomplex
  SConcHulp TNcomplex
  STempHulp TNcomplex
  s TNcomplex Complex Laplace variable
  Xx,Yy Real  Variables for graphs
  Xmax1,Xmin1 Real
  Xmax2,Xmin2 Real
  Ymax1,Ymin1 Real
  Ymax2,Ymin2 Real

G Procedure InputProcesParameters

Function: Input of process parameters Pe(m,s), Pe(m,a), Φ, Bi(m), Bi(h), μ, Pe(h,f), Pe(h,s), Γ, W_r, W_s, K1, K2, K3, Θ_s

Local Variables:
  ch Char

H Procedure FirstInverseLaplaceTransformForSIsZero

Function: Inverse Laplace transformation of the second Laplace domain function multiplied by s with respect to x by the method of residues for s=0

See Appendix C
I  Procedure FirstInverseLaplaceTransform

Function: Inverse Laplace transformation with respect to \( x \) by the method of residues

See Appendix B

J  Procedure ComplexFFT

Function: Complex inverse Fourier Transform

Heading:
In  Numpoints  Integer
In  Inverse  Boolean  True for inverse FFT
In  XReal, XImag  TNVectorPtr  Input array's
Out  XReal, XImag  TNVectorPtr  Output array's
Out  Error  Byte

K  Procedure CalculateSolid

Function: Calculation of \( Q(t) \) from \( K_1, K_2, K_3, U_s(t) \) and \( \Theta_s(t) \)

Heading:
In  K1,K2,K3,Numpoints,SConcReal,STempReal
Out  SolidReal

L  Procedure GraphicOutput

Function: Graphical output

Local Variables:
PlotRow  PlotArray  used for graphs
Ch

M  Procedure SetPlot

Function: Preparation of a plotarray for the time-functions

Heading:
In  YData  TNVectorPtr  Pointer vector with time-function
In  NulDate  TNcomplex  Stationary value
In  NumPlot  Integer
In  FirstX, LastX  Float  Time at first and last point
Out  Plot  PlotArray
Local Variables:
Increment Float Time interval between two points
XVal Float Time for actual point
Count Integer Counter

N Procedure Integrate

Function: Integration of the function in a plotarray

Heading:
In Numplot Integer
In plot Plotarray Function to be integrated
Out plot Plotarray Integrated function

Local Variables:
count Integer Counter
Save1,Save2 Float Help variables

O Procedure DiskOutput

Function: Output to disk

Heading:
In Numpoints, Numsmooth, Numplot, Ti, a, x, eta, dif, int,
FConcReal, FTempReal, SConcReal, STempReal, SolidReal,
FConcNul, FTempNul, SConcNul, STempNul, SolidNul

Local Variables:
OutFile String[14] Output file name
Out Text File variable
Ch Char
interval Integer
j Integer
count Integer
FConcSave1,2 Float
FTempSave1,2 Float
SConcSave1,2 Float
STempSave1,2 Float
SolidSave1,2 Float
nul Float


A-6
APPENDIX B  
Diagram and List of Procedures used for the 
First Inverse Laplace Transform (Unit FILT)

FirstInverseLaplaceTransform

NoTemperatureInIsotherm  A

CoefficientsMatrixSecondLaplaceDomain  B

NoHeatProduction  I

PolynomialsProduct  C1

Laguerre
Unit Laguer  E1

SortRoots  F1

Calculategf0gs0  J

CoefficientsNumeratorSecondLaplaceDomain  K

YInCoefficientsMatrix-
SecondLaplaceDomain  G1

YInElement  H1

CalculateNumeratorFirstLaplaceDomain  L

CalculateR2R3  M

YInCoefficientsMatrixSecondLaplaceDomain  G2

YInElement  H2

CalculateDenominatorFirstLaplaceDomainin  N

PolynomialsProduct  C2
Procedure FirstInverseLaplaceTransform

Function: Inverse Laplace transformation of $U_f(s,y)$, $\Theta_f(x,y)$, $U_s(s,y)$ and $\Theta_s(s,y)$ with respect to $x$ by the method of residues

Heading:
In $S,x,\eta,{PeMS},{PeMA},F_i,B_{iH},B_{iM},\mu,P_{eHF},P_{eHS},\Gamma,\omega,W_f,W_s,$ $K_1,K_2,K_3,\Theta_{iIn}$
Out $\text{FiltFConc}, \text{FiltFTemp}, \text{FiltSConc}, \text{FiltSTemp}$ $U_f(s,x), \Theta_f(s,x)$ $U_s(s,x), \Theta_s(s,x)$

Local Variables:
- Variable: Integer $U_f=1$, $\Theta_s=2$, $\Theta_f=3$
- Degree: Integer Degree of denominator polynomial $(s,x)$
- Tol: Float Tolerance for Laguerre's method
- Iter: TNIntVector Number of iterations in Laguerre's method
- MaxIter: Integer Maximum number of iterations in Laguerre's method
- NumRoots: Integer Number of roots found by Laguerre's method
- yPos, yneg: TNComplex Positive, negative roots
- $A,B,D,E,F,H,I$: TNComplex Matrix element coefficients of $1$, $y$ and $y^2$
- $\text{NEElement1}$, $\text{NEElement2}$, $\text{NEElement3}$: TNComplex Term 1, denominator $(s,y)$, Term 2, denominator $(s,y)$, Term 3, denominator $(s,y)$
- $\text{Coef}$: TNComplex Coefficients of denominator polynomial $(s,y)$
- $\text{coefficientsY6}$: TNComplex $\text{Coef}[6]$
- Error: Byte $b_0, g_{f0}$ and $g_{s0}$ residues
- $\text{Roots}$: TNComplex Roots of denominator $(s,y)$
- $\text{WortelArg}$, $\text{Wortel}$, $\text{CoshWortel}$, $\text{SinhWortel}$, $\text{WortelCoshWortel}$, $\text{NumFiS}$, $\text{DenomFiS}$, $\text{FiS}$, $j$, $\text{Scaling}$: TNComplex Numerator of $\Phi_s$, Denominator of $\Phi_s$ Counter Scaling factor of denominator $(s,y)$
A Procedure NoTemperatureInIsotherm

Function: Calculation of FiltFConc (Uf(s,x)) when K3=0

Heading:
In S,x
Out FiltFConc

Local Variables:
  hulp1,hulp2 TNcomplex Help variables

B Procedure CoefficientsMatrixSecondLaplaceDomain

Function: Calculation of matrix element coefficients for 1, y and y^2

Heading:
In S
Out FiS,A,B,D,E,F,H,I

C Procedure PolynomialsProduct

Function: Product of three 2nd degree polynomials

Heading:
In a,b,c
Out d

Local Variables:
  hulp TNcomplex

D Procedure PolynomialsSum

Function: Summation of three 2nd degree polynomials

Heading:
In a,b,c
Out d

Local variables:
  i Integer

E Procedure Laguerre

Function: Finding the roots of a complex polynomial

Modified version of the Turbo Pascal Numerical Methods Toolbox routine

Heading:
In Degree, Coef, Tol, MaxIter
Out Numroots, Roots, yRoots, iter, Error
F Procedure SortRoots

Function: Sort roots for positive or negative real part

Heading:
In  Roots  TNcompVector
In  n  Integer  Number of roots
Out ypos  TNcompVector  Positive roots
Out yneg  TNcompVector  Negative roots

Local Variables:
  i, ipos, ineg  Integer

G Procedure YInCoefficientsMatrixSecondLaplaceDomain

Function: Calculation of matrix elements for specified y-value

Heading:
In  y, A, B, D, E, F, H, I
Out  Aa, Be, De, Ee, eF, Ha, Ii

H Procedure YinElement

Function: Calculation of one matrix element for specified y

Heading:
In  y  TNcomplex
In  a  TNcompVector
Out  Aa  TNcomplex  a(0)+a(1)*y+a(2)*y^2

Local Variables:
  hulp  TNcomplex

I Procedure NoHeatProduction

Function: Calculation of FiltFTemp and FiltSTemp when \( r=0 \)

Heading:
In  S, x
Out  FiltFTemp, FiltSTemp

Local Variables:
  hulp, hulpl, hulp2  TNcomplex
  one  TNcompVector
  j, variable  Integer
  Num, Denom  TNcomplex
  coefficientY4  TNcomplex
J Procedure Calculategf0gs0

Function: Calculation of \( g_{10} \) and \( g_{s0} \) from boundary conditions

Heading:
In ypos, S, FiS, A, B, D, E, F, H, I
Out gf0, gs0

Local variables:
- \( j, t \) Integer
- CoefGf0, CoefGs0, Konst TNcompVector
- hulp1, hulp2 TNcomplex
- Coef1Gf2Gs, Coef2Gf1Gs, Coef1GfK2, Coef2GfK2, Coef1GsK2, Coef2GsK2 TNcomplex
- CoefGfO\[1\].CoefGsO\[2\], CoefGfO\[2\].CoefGsO\[1\], CoefGfO\[1\].Konst\[2\], CoefGfO\[2\].Konst\[1\], CoefGsO\[1\].Konst\[2\], CoefGsO\[2\].Konst\[1\]

K Procedure CoefficientsNumeratorSecondLaplaceDomain

Function: Calculation of the coefficients of \( g_{10} \) and \( g_{s0} \) and the constant part in the second Laplace domain

Heading:
In \( j \) Integer \( \theta_s = 2, \theta_r = 3 \)
In \( y \) TNcomplex
In \( S \) TNcomplex
In \( FiS \) TNcomplex
In A, B, D, E, F, H, I TNcompVector
Out CoefGf0 TNcomplex Coefficient of \( g_{10} \)
Out CoefGs0 TNcomplex Coefficient of \( g_{s0} \)
Out Konst TNcomplex Constant part

Local variables:
- Aa, Be, De, Ee, Ef, Ha, Ii TNComplex
  - Matrix elements for specified \( y \)

L Procedure CalculateNumeratorFirstLaplaceDomain

Function: Calculation of the numerator of the First Laplace domain \((s, x)\)

Heading:
In variable, y, A, B, D, E, F, H, I, gf0, gs0
Out Num TNcomplex Numerator\((s, y)\)

Local Variables:
- Aa, Be, De, Ee, Ef, Ha, Ii TNComplex
  - Matrix elements for specified \( y \)
- R2, R3 TNcomplex
M Procedure CalculateR2R3
Function: Calculation of R2 and R3

Heading:
In y,S,gfO,gsO
Out R2,R3

Local Variables:
one, theta, hulp TNcomplex

N Procedure CalculateDenominatorFirstLaplaceDomain
Function: Calculation of the denominator of the first Laplace domain

Heading:
In ypos,ypos,yneg,CoefficientY4
Out Denom TNcomplex Denominator(s,x)

Local Variables:
yhulp TNcomplex
hulpl,hulp2,hulp3 TNcomplex

O Procedure Calculateb0gfOGsO
Function: Calculation of b0, gfO and gsO from boundary conditions

Heading:
In ypos,S,FiS,A,B,D,E,F,H,I
Out b0,gf0,gs0

Local variables:
  j,t Integer
  Matrix TNcompMatrix
  Konst TNcompVector
  Solution TNcompVector
  error Byte
  hulpl,hulp2 TNcomplex

P Procedure CoefficientsNumeratorSecondLaplaceDomain
Function: Calculation of the coefficients of b0, gfO and gsO and the constant part in the second Laplace domain numerator

Heading:
In j Integer U_f=1, n_s=2, r_f=3
In y TNcomplex
In S TNcomplex
In FiS TNcomplex
In A,B,D,E,F,H,I TNcompVector
Out CoefBO TNcomplex Coefficient of b0
Out CoefGs0 TNcomplex Coefficient of gfO
Out CoefGf0 TNcomplex Coefficient of $g_{s0}$
Out Konst TNcomplex Constant part

Local Variables:
- Aa, Be, De, Ee, eF, Ha, Ii TNcomplex Matrix elements for specified $y$
- R1Konst, R1CoefB0 TNcomplex
- R2Konst, R2CoefGs0 TNcomplex
- R3Konst, R3CoefGf0 TNcomplex
- hulp1, hulp2 TNcomplex

Q Procedure R1R2R3Coefficients

Function: Calculation of coefficients of $b_0$, $g_{f0}$ and $g_{s0}$ in R1, R2 and R3

Heading:
- In y TNcomplex
- Out R1Konst TNcomplex Constant part in R1
- Out R1CoefB0 TNcomplex Coefficient of $b_0$ in R1
- Out R2Konst TNcomplex Constant part in R2
- Out R2CoefGs0 TNcomplex Coefficient of $g_{s0}$ in R2
- Out R3Konst TNcomplex Constant part in R3
- Out R3CoefGf0 TNcomplex Coefficient of $g_{f0}$ in R3

Local Variables:
- one, theta TNcomplex

R Procedure Gaussian_elimination

Function: Gauss method for solving a matrix equation

Modified version of the Turbo Pascal Numerical Methods Toolbox routine

Heading:
- In Dimen Integer Dimension
- In Coefficients TNmatrix Square coefficients matrix
- In Constants TNvector Constant terms
- Out Solution TNvector Solution of equations
- Out Error Byte

S Procedure CalculateResidues

Function: Calculation of residues

Heading:
- In Variable, ypos, yneg, S, x, FiS
- A, B, D, E, F, H, I, CoefficientY6
- Out residu TNcompvector

Local variables:
- Num, Denom TNcomplex
- j Integer
- hulp TNcomplex
T Procedure CalculateNumeratorFirstLaplaceDomain

Function: Calculation of the numerator of the first Laplace domain \((s,x)\)

Heading:
In \(y, S, A, B, D, E, F, H, I, b_0, g_0, g_s\)
Out \(\text{Num} \quad \text{TNcomplex} \quad \text{Numerator of first Laplace domain}\)

Local variables:
- \(A, B, D, E, E, e, F, H, I, i\) \(\text{TNcomplex} \quad \text{Matrix elements for specified } y\)
- \(R_1, R_2, R_3 \quad \text{TNcomplex}\)

U Procedure CalculateR1R2R3

Function: Calculation of \(R_1, R_2 \text{ and } R_3\)

Heading:
In \(y, S, b_0, g_0, g_s\)
Out \(R_1, R_2, R_3\)

Local Variables:
- \(\text{One, theta, hulp TNcomplex}\)

V Procedure CalculateDenominatorFirstLaplaceDomain

Function: Calculation of the denominator of the first Laplace domain

Heading:
In \(i \quad \text{Integer}\)
In \(y_{pos}, y_{neg} \quad \text{TNcompVector}\)
In \(\text{CoefficientY6} \quad \text{TNcomplex}\)
Out \(\text{Denom} \quad \text{TNcomplex} \quad \text{denominator } (s,x)\)

Local Variables:
- \(y_{hulp1}, y_{hulp2} \quad \text{TNcomplex}\)
- \(hulp1, hulp2, hulp3 \quad \text{TNcomplex}\)

============================================================================
W Procedure CalculateFirstInverseLaplaceTransformOfSConc

Function: Calculation of FiltSConc (U_a(s,x))

Heading:
In S, eta, FiltFConc, FiltSTemp
Out FiltSConc

Local variables:
- FiltA : TNcomplex
- WortelArg : TNcomplex
- Wortel : TNcomplex
- SinhEtaWortel : TNcomplex

- A(s,x)
APPENDIX C  Diagram and list of Procedures used for the First Inverse Laplace Transform for s=0 (Unit FILTNull)

FirstInverseLaplaceTransformForSIsZero

CoefficientsMatrixSecondLaplaceDomain A

PolynomialsProduct B

Laguerre C
  Unit Laguer

SortRoots D

Calculategf0gs0 G

CoefficientsNumeratorSecondLaplaceDomain H

YInCoefficientsMatrixSecondLaplaceDomain E1
  YinElement F1

Gf0Gs0InNumeratorSecondLaplaceDomain I

CoefficientsNumeratorSecondLaplaceDomain J

YInCoefficientsMatrixSecondLaplaceDomain E2
  YinElement F2

CalculateDenominatorFirstLaplaceDomain K
Procedure FirstInverseLaplaceTransformForSIsZero

Function: Inverse Laplace transformation of the second Laplace domain functions $U_r(s,y)$, $\Theta_r(s,y)$, $U_s(s,y)$ and $\Theta_s(s,y)$, multiplied by $s$ with respect to $x$ by the method of residues for $s=0$

Heading:
In $x, \eta, PeMS, PeMA, Fi, BiM, BiH, Mu, PeHF, PeHS, Gamma, Wf, Ws, K1, K2, K3, \Thetaeta$ 
Out FiltFTemp, FiltSTemp $\Theta_r(s,x), \Theta_s(s,x)$

Local Variables:
- Variable
- Degree Integer
- Tol Float
- Iter TNIntVector
- MaxIter Integer
- NumRoots Integer
- yRoots TNcompVector
- ypos, yneg TNcompVector
- A, B, D, E, F, H, I TNcompVector
- NElement1 TNcompVector
- NElement2 TNcompVector
- NElement3 TNcompVector
- Coef TNcompVector
- coefficientY4 TNcomplex
- Error Byte
- residu TNcompVector
- Roots TNcompVector
- Num, Denom TNcomplex
- hulp TNcomplex
- FiS TNcomplex
- gf0, gs0 TNcomplex
- j Integer
- one TNcompVector
- Scaling Float

\[ s = 1, 2 \]

\[ \text{Degree of denominator polynomial (s,x)} \]

\[ \text{Tolerance for Laguerre's method} \]

\[ \text{Number of iterations in Laguerre's method} \]

\[ \text{Maximum number of iterations in Laguerre's method} \]

\[ \text{Number of roots found by Laguerre's method} \]

\[ \text{Function value's at roots} \]

\[ \text{Positive, negative roots} \]

\[ \text{Matrix element coefficients of 1, y and y^2} \]

\[ \text{Term 1, denominator(s,y)} \]

\[ \text{Term 2, denominator(s,y)} \]

\[ \text{Term 3, denominator(s,y)} \]

\[ \text{Coefficients of denominator polynomial (s,y)} \]

\[ \text{Coefficient Y4} \]

\[ \text{Error} \]

\[ \text{Residu} \]

\[ \text{Roots} \]

\[ \text{Num, Denom} \]

\[ \text{Hulp} \]

\[ \text{FiS} \]

\[ \text{Gf0, gs0} \]

\[ \text{J} \]

\[ \text{One} \]

\[ \text{Scaling} \]

\[ \text{Scaling factor of denominator} \]

===================================================================
A Procedure CoefficientsMatrixSecondLaplaceDomain

Function: Calculation of matrix element coefficients for 1, y and $y^2$

Heading:
In $s$
Out FiS, A, B, D, E, F, H, I

======================================================================

C-2
B Procedure PolynomialsProduct

Function: Product of three 2nd degree polynomials

Heading:
In a,b,c TNcompVector
Out d TNcompVector

Local Variables:
  hulp TNcomplex

C Procedure Laguerre

Function: Finding the roots of a complex polynomial

Modified version of the Turbo Pascal Numerical Methods Toolbox routine

Heading:
In Degree, Coef, Tol, Maxiter, Numroots, Roots, yRoots, iter, Error

D Procedure SortRoots

Function: Sort roots for positive or negative real part

Heading:
In Roots TNcompVector
In n Integer Number of roots
Out ypos TNcompVector Positive roots
Out yneg TNcompVector Negative roots

Local Variables:
i, ipos, ineg Integer

E Procedure YInCoefficientsMatrixSecondLaplaceDomain

Function: Calculation of matrix elements for specified y-value

Heading:
In y,A,B,D,E,F,H,I
Out Aa,Be,De,Ee,eF,Ha,Ii

F Procedure YinElement

Function: Calculation of one matrix element for specified y

Heading:
In y TNcomplex
In a TNcompVector
Out Aa TNcomplex a(0)+a(1)*y+a(2)*y^2
Local Variables:
- hulp
- TNcomplex

G Procedure Calculate gfO.gsO

Function: Calculation of $g_{r0}$ and $g_{s0}$ from boundary conditions

Heading:
In ypos, S, FiS, A, B, D, E, F, H, I
Out gf0, gs0

Local variables:
- j, t
- CoefGf0
- CoefGs0
- Konst
- hulp1, hulp2
- Coef1Gf2Gs
- Coef2Gf1Gs
- Coef1GfK2
- Coef2GfK1
- Coef1GsK2
- Coef2GsK1

H Procedure CoefficientsNumeratorSecondLaplaceDomain

Function: Calculation of the coefficients of $g_{r0}$ and $g_{s0}$ and the constant part in the second Laplace domain

Heading:
In j
In y
In S
In FiS
In A, B, D, E, F, H, I
Out CoefGf0
Out CoefGs0
Out Konst

Local variables:
- Aa, Be, De, Ee, Ef, Ha, Ii

I Procedure CalculateNumeratorFirstLaplaceDomain

Function: Calculation of the numerator of the First Laplace domain ($s,x$)

Heading:
In variable, y, A, B, D, E, F, H, I
Out Num

C-4
Local Variables:
Aa, Be, De, Es, eF, Ha, Ii TNcomplex
R2, R3 TNcomplex

Procedure CalculateR2R3

Function: Calculation of R2 and R3

Heading:
In y, S, gf0, gs0
Out R2, R3

Local Variables:
one, theta, hulp TNcomplex

Procedure CalculateDenominatorFirstLaplaceDomain

Function: Calculation of the denominator of the first Laplace domain

Heading:
In i, ypos, yneg, CoefficientY4
Out Denom TNcomplex

Local Variables:
yhulp TNcomplex
hulp1, hulp2, hulp3 TNcomplex
APPENDIX D  COMPARISON OF EXECUTION TIME AND ACCURACY FOR A BREATHTHROUGH CURVE

Process Parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
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<tbody>
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<td>5.0</td>
</tr>
<tr>
<td>( Pe(m,a) )</td>
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<td>( Bi(m) )</td>
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<td>( Pe(h,f) )</td>
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<td>( \phi )</td>
<td>1000.0</td>
</tr>
<tr>
<td>( Bi(h) )</td>
<td>50.0</td>
</tr>
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</table>

\[ \Gamma = 0.002 \quad W_f = 0.5 \quad W_a = 0.5 \quad K_1 = 0.0 \quad K_2 = 5000.0 \quad K_3 = -1000.0 \quad \theta_{1_a} = 0.5 \]

Fluid Concentration:

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<th>Number of Points</th>
<th>( N = 32 )</th>
<th>( N = 64 )</th>
<th>( N = 256 )</th>
<th>( N = 1024 )</th>
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</thead>
<tbody>
<tr>
<td>Execution Time (s)</td>
<td>18.90</td>
<td>34.30</td>
<td>128.60</td>
<td>506.70</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \tau )</th>
<th>( U_f(\tau) )</th>
<th>( U_f(\tau) )</th>
<th>( U_f(\tau) )</th>
<th>( U_f(\tau) )</th>
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## Fluid Temperature:

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Figure E.1 Cylinder in a slice of a reactor for which mass and heat balances are calculated
APPENDIX E  MODEL EQUATIONS FOR A NON-ISOTHERMAL FIXED-BED REACTOR WITH RADIAL GRADIENTS

Although radial gradients are not included in the program, the model equations will be given here for reactors with radial gradients of concentrations and temperatures.

E.1 Mass balance for the fluid phase

The radial dispersion coefficient is given by \( D_p \). The balance for a cylinder in a slice of the reactor (figure E.1) can then be written as (see (3.2)):

\[
\begin{align*}
\nu \left[ \frac{\partial C_f}{\partial z} \right]_{t,r} - D_a \left[ \frac{\partial^2 C_f}{\partial z^2} \right]_{t,r} - \frac{D_r}{r} \frac{\partial}{\partial r} \left[ \frac{\partial C_f}{\partial r} \right]_{z,t} \\
+ \frac{\partial C_f}{\partial t} \left( \frac{3D_p(1-\varepsilon)}{R_p \varepsilon} \right) \frac{\partial C_s}{\partial r} r_p = 0 \quad (E.1)
\end{align*}
\]

E.2 Mass balance in a particle

Equation (3.4) will not be changed by introduction of radial gradients:

\[
\frac{D_p}{r_p^2} \frac{\partial}{\partial r} \left[ r_p^2 \frac{\partial C_s}{\partial r} \right]_{t,z,r} = \left[ \frac{\partial q}{\partial t} \right]_{r_p,z,r} \quad (E.2)
\]

E.3 Heat balance for the fluid phase

With introduction of the radial heat conduction coefficient of the fluid, \( \lambda_{fr} \), equation (3.6) becomes:

\[
\begin{align*}
\nu \cdot \rho_f \cdot C_p \frac{\partial T_f}{\partial z} \left[ \frac{\partial^2 T_f}{\partial z^2} \right]_{t,r} - \lambda_{fz} \frac{\partial^2 T_f}{\partial z^2} \left[ \frac{\partial T_f}{\partial r} \right]_{z,t} - \frac{\lambda_{fr}}{r} \frac{\partial}{\partial r} \left[ \frac{\partial T_f}{\partial r} \right]_{z,t} \\
+ C_p \cdot \rho_f \frac{\partial T_f}{\partial t} \left( T_s - T_f \right) = h_f \cdot \frac{3}{R_p} \frac{(1-\varepsilon)}{\varepsilon} \cdot (T_s - T_f) \quad (E.3)
\end{align*}
\]
E.4 Heat balance for the solid phase

Introduction of the radial heat conduction coefficient, $\lambda_s r$, the solid temperature balance for a cylinder is given by (see (3.8)):

$$
\frac{3}{R_p}(T_s - T_f) - \lambda_s a \left[ \frac{\delta^2 T_s}{\delta z^2} \right]_{t,r} - \frac{\lambda_s \delta}{r} \frac{\partial}{\partial r} \left[ \frac{\partial T_s}{\partial r} \right]_{z,t}
$$

$$
+ C_p S \cdot \rho_s \left[ \frac{\partial T_s}{\partial t} \right]_{z,r} = (-\Delta H) \frac{\partial q}{\partial t} = (-\Delta H) \frac{3}{R_p} D_p \left[ \frac{\partial c_s}{\partial r_p} \right]_{r_p=R_p}
$$

(E.4)

E.5 Boundary and initial conditions

$$
\frac{\partial c_f}{\partial z} \bigg|_{z=0^+} = \frac{v}{D_a} \left[ c_f \bigg|_{z=0^+} - c_f \bigg|_{z=0^-} \right] \quad c_f \bigg|_{z \rightarrow \infty} = 0
$$

(E.5)(E.6)

$$
\frac{\partial c_f}{\partial r} \bigg|_{r=0} = 0 \quad \frac{\partial c_f}{\partial r} \bigg|_{r=R} = 0 \quad c_f \bigg|_{t=0} = 0
$$

(E.7)(E.8)(E.9)

$$
\frac{\partial c_s}{\partial r_p} \bigg|_{r_p=R_p} = \frac{k_f}{D_p} (c_f - c_s) \quad (E.10)
$$

$$
\frac{\partial c_s}{\partial r_p} \bigg|_{r_p=0} = 0 \quad c_s \bigg|_{t=0} = 0
$$

(E.11)(E.12)

$$
\frac{\partial T_f}{\partial z} \bigg|_{z=0^+} = \frac{\nu \cdot \rho_s \cdot C_p f}{\lambda f_a} \left[ T_f \bigg|_{z=0^+} - T_f \bigg|_{z=0^-} \right]
$$

$$
T_f \bigg|_{z \rightarrow \infty} = 0 \quad T_f \bigg|_{t=0} = T_{wa}\quad (E.13)
$$

$$
\frac{\partial T_f}{\partial r} \bigg|_{r=0} = 0 \quad \frac{\partial T_f}{\partial r} \bigg|_{r=R} = \frac{h_w f}{\lambda f_r} (T_w - T_f)
$$

(E.14)(E.15)(E.16)(E.17)

E-2
\[
\frac{\delta T_s}{\delta z} \bigg|_{z=0^+} = 0 \quad T_s \bigg|_{z \to \infty} = 0 \quad (E.18) \quad (E.19)
\]

\[
T_s \bigg|_{t=0} = T_{\text{wall}} \quad (E.20)
\]

\[
\frac{\delta T_s}{\delta r} \bigg|_{r=0} = 0 \quad \frac{\delta T_s}{\delta r} \bigg|_{r=R} = \frac{h_{\text{ws}}}{\lambda r} (T_w - T_s) \quad (E.21) \quad (E.22)
\]

Because of the introduction of four parameters, \( r, D_r, \lambda_{fr} \) and \( \lambda_{sr} \), three new dimensionless number have to be introduced. These are chosen as:

\[
\sigma = \frac{r}{R}
\]

\[
\text{Pe}(m, r) = \frac{R^2 v}{L D_r}
\]

\[
\text{Pe}(h, f, r) = \frac{R^2 v \rho_f C_{pf}}{L \lambda_{fr}}
\]

\[
\text{Pe}(h, s, r) = \frac{R^2 v \rho_s C_{ps}}{L \lambda_{sr}}
\]

With these parameters, the model equations (E.1)-(E.22) can be written in dimensionless form as follows:

**Fluid mass balance**

\[
\begin{align*}
\frac{\partial U_f}{\partial x} & \bigg|_{\tau, \sigma} - \frac{1}{\text{Pe}(m, a)} \frac{\partial^2 U_f}{\partial x^2} \bigg|_{\tau, \sigma} - \frac{1}{\text{Pe}(m, r)} \frac{1}{\sigma} \frac{\partial U_f}{\sigma} \bigg|_{x, \tau} \\
+ \frac{\partial U_f}{\partial \tau} \bigg|_{x, \sigma} + \frac{1}{\text{Pe}(m, s)} \frac{3 \mu}{\eta} \frac{\partial U_s}{\partial \eta} \bigg|_{\eta=1} & = 0 \quad (E.23)
\end{align*}
\]

**Particle mass balance**

\[
\frac{\partial Q}{\partial \tau} \bigg|_{\eta, x, \sigma} = \frac{1}{\text{Pe}(m, s)} \left[ \frac{\partial^2 U_s}{\partial \eta^2} + \frac{2}{\eta} \frac{\partial U_s}{\partial \eta} \right] \bigg|_{\tau, x, \sigma} \quad (E.24)
\]

E-3
Isotherm

\[ Q = K_1 + K_2 U_s + K_3 \theta_s \]  

(E.25)

Fluid heat balance

\[
\frac{\partial \theta_f}{\partial x} \tau, \sigma - \frac{1}{Pe(h,f)} \frac{\partial^2 \theta_f}{\partial x^2} \tau, \sigma - \frac{1}{Pe(w,f,r)} \frac{\partial}{\partial \sigma} \left[ \frac{\partial \theta_f}{\partial \sigma} \right] x, \tau + \frac{\partial \theta_f}{\partial \tau} x, \sigma \]

\[ + \frac{3 \cdot Bi(h)}{Pe(h,s)} \Phi \mu (\theta_s - \theta_f) = 0 \]  

(E.26)

Solid heat balance

\[ \frac{1}{Pe(h,s)} \frac{\partial^2 \theta_s}{\partial x^2} \tau, \sigma - \frac{1}{Pe(w,s,r)} \frac{\partial}{\partial \sigma} \left[ \frac{\partial \theta_s}{\partial \sigma} \right] x, \tau + \frac{\partial \theta_s}{\partial \tau} x, \sigma \]

\[ + \frac{3 \cdot Bi(h)}{Pe(h,s)} (\theta_s - \theta_f) - \frac{3 \cdot \Gamma}{Pe(m,s)} \frac{\partial U_s}{\partial \eta} \eta=1 = 0 \]  

(E.27)

Boundary conditions

Fluid mass balance

\[
\frac{\delta U_f}{\delta x} \bigg|_{x=0^+} = Pe(m,a) \left[ U_f \bigg|_{x=0^+} - U_f \bigg|_{x=0^-} \right] U_f \bigg|_{x \to \infty} = 0
\]

(E.28)

\[ \frac{\delta U_f}{\delta \sigma} \bigg|_{\sigma=0} = 0 \quad \frac{\delta U_f}{\delta \sigma} \bigg|_{\sigma=1} = 0 \quad U_f \bigg|_{\tau=0} = 0 \]

(E.29) (E.30) (E.31) (E.32)

Particle mass balance

\[ \frac{\delta U_s}{\delta \eta} \bigg|_{\eta=1} = Bi(m) \left[ U_f - U_s \bigg|_{\eta=1} \right] \]

(E.33)

E-4
\[ \frac{\partial U_s}{\partial \eta} \bigg|_{\eta=0} = 0 \quad U_s \bigg|_{\tau=0} = 0 \quad (E.34) (E.35) \]

**Fluid heat balance**

\[ \frac{\partial \theta_f}{\partial x} \bigg|_{x=0^+} = Pe(h,f) \left[ \theta_f \bigg|_{x=0^+} - \theta_f \bigg|_{x=0^-} \right] \quad (E.36) \]

\[ \theta_f \bigg|_{x \to \infty} = 0 \quad \theta_f \bigg|_{\tau=0} = 0 \quad (E.37) (E.38) \]

\[ \frac{\partial \theta_f}{\partial \sigma} \bigg|_{\sigma=0} = 0 \quad \frac{\partial \theta_f}{\partial \sigma} \bigg|_{\sigma=1} = Bi(w,f)(-\theta_f) \quad (E.39) (E.40) \]

**Solid heat balance**

\[ \frac{\partial \theta_s}{\partial x} \bigg|_{x=0^+} = 0 \quad \theta_s \bigg|_{x \to \infty} = 0 \quad (E.41) (E.42) \]

\[ \theta_s \bigg|_{\tau=0} = 0 \quad (E.43) \]

\[ \frac{\partial \theta_s}{\partial \sigma} \bigg|_{\sigma=0} = 0 \quad \frac{\partial \theta_s}{\partial \sigma} \bigg|_{\sigma=1} = Bi(w,s)(-\theta_s) \quad (E.44) (E.45) \]