Master Thesis

Limit cycles in homogeneous azeotropic distillation

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Limit Cycles in Homogeneous Azeotropic Distillation

Diploma Thesis

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Chapter 1

Introduction

Separation processes are probably the most challenging task in process engineering. Considering their importance in industry it makes them a very attractive field of research. Amongst the commonly implemented separation processes distillation is presumably the most widely used.

Despite its importance, distillation and its dynamic behaviour is still not completely understood. Due to the complex nature of the process, the models used to describe distillation processes are very non linear. As a consequence their solution is a very demanding problem. In fact, for instance output multiplicities have been predicted and afterwards validated through both simulations and experiments. When investigating this phenomenon in the last few years, it has been found that limit cycle behaviour exist for homogeneous azeotropic distillation. This aspect has been validated through simulations. However, the experimental validation is still missing.

This work is thought to contribute to a prospective experimental validation and to the understanding of the dynamic effects, which lead to limit cycle behaviour. To accomplish this task, extensive and detailed numerical simulations have been run and qualitative analysis has been performed.

This work will be structured into three main parts. First the reader is provided with the theoretical background and the tools necessary for the further understanding. Thereafter detailed dynamic analysis of limit cycle behaviour is provided. This analysis may itself be divided in several parts as it will be seen in the structuring of the chapters. Finally conclusions are drawn and recommendations towards a future experimental set-up are given.
Chapter 2

Theoretical Background

In this work many well established concepts, ideas and models are the basis for the investigations. In order to provide some insight into those areas a short theoretical overview is given here. This theoretical background is by no means complete but shall provide a reader who is new to the topic of this work with some information which is essential for the understanding.

The chapter is organized as follows. First the concepts of distillation as well as a short introduction into residue curves will be given. Furthermore the notion of a distillation column is introduced and an overview over the different column models is provided. During that overview, emphasis will be set on the assumptions which are necessary for the according models. Finally a connection is drawn to models implemented in the simulation package used. Complex phenomena like multiple steady states, bifurcation and limit cycle behaviour will only be introduced in the next chapter.

2.1 Distillation

The goal of distillation is to separate a mixture of several components. The principle of that separation in distillation lies in the production of an additional phase with a difference in composition compared to the original one and to exploit this difference to drive the composition of the product subsequently into the desired direction. To achieve a split into two different phases thermal energy is used to provide the energy needed to generate the new phase and to compensate for the entropy of mixing.

Often the mixture to be separated with distillation is liquid. Therefore the additional phase created is a vapor phase generated through evaporation of the liquid phase. The contact between the two phases allows for mass and heat transfer. If the contact time is long enough the two phases will reach an equilibrium, where neither heat nor mass transfer will occur anymore. This state is called the vapor-liquid equilibrium (VLE). In general the VLE implies different compositions in the two phases: while the vapor will be richer on the more volatile components, the liquid will contain more of the less volatile components.

Now the vapor may be drawn off and liquified, i.e. condensed, again to form a new liquid phase of different composition, which is richer in the more volatile species in the mixture. This procedure may be subsequently repeated with an enrichment of the mixture in the more volatile components, which would finally result in a pure component after an infinite number of separations.
However this principle does not always work since there may be points where there is no difference in composition between the liquid and the vapor phase. Such points always occur at the pure components, which is no problem, since there is no need for a separation. On the other hand there are points called azeotropes where such behaviour may be observed for mixtures. In such a case the vapor obtained is identical to the liquid and it is not possible any more to have a change in composition as it would be needed to achieve a separation into the pure components. In order to deal with this situation different approaches are possible. A commonly applied principle would be to add an additional component and to use several distillation columns. In this case the separation is performed working around the azeotrope where no separation is possible. More details regarding that topic may be found in the specific literature. The reader is referred to the concise book of Stichlmair and Fair (Stichlmair and Fair 1998).

In the next subsection we first consider the simple distillation unit. A still containing a mixture is heated and the vapor produced is drawn off. We will describe the evolution of the liquid composition in the still in order to introduce the concept of residue curves. Then the basic properties of residue curves will be presented. Later the connection between those residue curves and the analysis of multiple steady states and limit cycle behaviour will be shown.

2.1.1 Simple Distillation

Consider a still containing a mixture at composition \( x \) to be separated. It is assumed that the mixture is at its bubble point. A hold up \( M \) is considered. If this still is constantly heated with a heat flux \( Q \) it will start to boil and obviously a vapor stream \( V \) at composition \( y \) will leave that still. The system described so far is illustrated in Figure 2.1. The equations describing the dynamic evolution of the concentrations in the still will now be developed. A simple material balance over each component \( i \) leads to the following expression, where \( n_c \) is the number of components:

\[
\frac{d}{dt}(M x_i) = -V y_i(x) \quad i = 1, \ldots, n_c
\]  

(2.1)
The total differential in time may now be expanded to lead to the following expression:

$$M \frac{d}{dt} x_i + x_i \frac{d}{dt} M = -V y_i (x) \quad i = 1, \ldots, n_c \quad (2.2)$$

Based on the definition of mole fractions, they have to add up to unity in both phases, the liquid and the vapor:

$$\sum_{i=1}^{n_l} x_i = \sum_{i=1}^{n_v} y_i = 1 \quad (2.3)$$

Adding up Equation 2.1 over all components and considering the condition stated in Equation 2.3 the total material balance follows.

$$\frac{d}{dt} M = -V \quad (2.4)$$

This total material balance could have been derived directly from the system, too. The substitution of the total material balance (2.4) into the set of material balances over single components (2.1) leads to a simplification which is displayed in the following expression.

$$\frac{d}{dt} x_i = -\frac{V}{M} (y_i (x) - x_i) \quad i = 1, \ldots, n_c \quad (2.5)$$

This expression can be further simplified. Looking at the quantity \( \frac{V}{M} \) it is noticed that its dimension is time and this time has to be somehow characteristic to the system. Unfortunately the two quantities \( M \) and \( V \) are not constant, so it’s not possible to specify a characteristic time for the process in total, but only for any point in time. Nevertheless this characteristic time is used to apply a fold onto our integration variable, the physical time. A dimensionless, ("warped") time \( \xi \) is defined as:

$$\xi = \frac{V}{M} t \quad (2.6)$$

Substituting this warped time into the differential, single component mass balances (2.1) finally a simple looking, autonomous and very famous equation may be obtained, the residue curve equation:

$$\frac{d}{d\xi} x_i = y_i (x) - x_i \quad i = 1, \ldots, n_c \quad (2.7)$$

This equation describes the evolution of \( x_i \) with \( \xi \). The evolution and change in \( \xi \) is given by the energy balance, which is not explicitly written in terms of \( \xi \) though:

$$\frac{d}{dt} (M h_L (x)) = -V h_V (y (x)) + Q (t) \quad i = 1, \ldots, n_c \quad (2.8)$$

Please note that \( h_L \) and \( h_V \) are the specific enthalpies of the liquid (L) and the vapor (V) phase respectively and depend on composition.

This whole set of equations defines the evolution of the liquid (residue) concentration in the still. This evolution will be smooth in time an will follow a characteristic path. This path is characteristic for every starting point and is usually called a residue curve.
2.1.2 Residue Curve Maps

In this work it is dealt with ternary mixtures, thus let’s assume a ternary mixture for the following. Now the residue curves, calculated as described in the previous section, may be plotted into the the composition space defined by the triangular composition diagram, starting from an arbitrary initial composition and applying Equation 2.7 to calculate their evolution. Repeating this procedure a set of residue curves is obtained. The diagram with the residue curves is now called residue curve map and describes the characteristic behaviour of any mixture of the corresponding three components. An example of such a residue curve diagram can be found in Figure 2.2.

Residue curve diagrams show the characteristic behaviour of a mixture and provide useful properties which were described in an famous article by (Doherty and Perkins 1978). This characteristic behaviour can be proven by applying the theory of dynamical systems and topology to the residue curve equation. Here we will just report the most important results, for further information the reader is referred to (Doherty and Perkins 1978).

The equilibria of that equation, i.e. the solutions of $y(x) - x = 0$, result in singular points of a residue curve diagram. These points, which are the pure components and the azeotropes in the composition space play an important role for the analysis of residue curve diagrams and the interaction of the components. The singular points may be categorized into three groups which all have real nonzero eigenvalues: stable nodes with all eigenvalues negative, unstable nodes with all eigenvalues positive and saddles with both positive and negative eigenvalues. Generally speaking residue curves evolve from unstable nodes and end at stable nodes while at saddles both, starting and ending residue curves will be found. One of the most important features of residue curves is that they do not intersect and there will be no closed cycles.

If we go back to the derivation of the residue curve equation, we will see, that at constant pressure temperature will increase with time and thus along a residue curve. This increase is expected to be monotonously as with time more and more of the mixture is boiled of and the residue is enriched in the components of low volatility. When looking at this dynamic behaviour it becomes clear that unstable nodes must represent local minima in terms of boiling point temperatures, whereas stable nodes must represent local maxima. Generally, based upon the features described before it is clear that
the singular point with the globally highest boiling point is always an unstable and the one with the globally lowest boiling point is always a stable node.

It was just shown, that the residue curves describe the evolution of the liquid composition in the residues of a mixture subject to evaporation. The importance of these curves is not only based on that description, but there is a close relationship to internal profiles in distillation columns. This effect will be explained and described in Section 2.5 after having introduced the concepts and models for distillation columns.

2.2 Distillation Columns

2.2.1 A Conceptual Approach

In Section 2.1 the concept of distillation was introduced and a model for simple distillation was developed in Section 2.1.1. However the process described so far is not practical yet since the degree of separation which can be achieved might not be sufficient for the degree of separation desired.

Nevertheless simple distillation may be operated several times in a row in order to achieve better results. Thus the generated vapor phase from the first step may be condensed again and this condensed phase may now be subject to a further distillation process. With every step added the product will become enriched more and more in the light component, finally fulfilling the requirements.

This is still not the best way to operate such a separation, since we are producing loads of liquid residue. A solution to that problem is to operate the series of distillations countercurrently and continuously. Thus the vapor produced in one unit is condensed again and fed to the next distillation unit, while the residue is taken off and fed to the previous unit. The feed would then be somewhere in the middle. The process sketched here is not really effective, since lots of energy is wasted in the subsequent evaporation and condensation steps and on the other side for every step a distillation unit would be needed.

The solution to those ineffective operation is a distillation column, where several stages, one above the other, which all work as simple distillation units are interconnected directly. The heat for evaporation is provided directly by the heat of condensation, the withdrawal of liquid phase of one stage and the outflow of the vapor are favored by gravity. A simple sketch of such a unit can be seen in Figure 2.3. As we can see, the vapor can rise in the column an pass through the different trays, whereupon it is in close contact with the liquid on that tray. During that contact mass transfer and heat transfer are occurring and a VLE is approached. The liquid holdup on a tray is ensured through a weir over which the liquid flows to next lower section. This set-up is called a tray column.

Another possibility to operate a distillation column would be to fill it with a packing instead of the trays. The liquid would then flow down along the surface of the packing where it would be in close contact with the vapor stream rising in the column. This kind of column is called a packed column.

In the following subsections models for tray distillation columns are introduced. First a detailed model will be derived and lateron this will be simplified to obtain finally the constant molar overflow model. Furthermore the assumptions for all the models are collected and explained in detail. After that a model for a packed column is presented.
2.2.2 A detailed column model

Most investigations and analysis done are based on models of tray columns since it makes handling of the models and their derivation in mathematical terms much easier. Furthermore the mathematical model obtained is less complicated and the numerical solution is simplified. Nevertheless in a later section the model for packed columns will be derived, since this model will be used to verify results obtained by models for tray columns.

To start consider a single stage of the column. A schematic drawing for that stage is given in Figure 2.4. The first equations to write are the material balances:
In these material balances $F^k$ indicates the feed stream entering stage $k$ whereas $V$ and $L$ are vapor and liquid streams entering a stage, respectively. $W$ and $U$ denote side streams leaving the system. Finally $x$ and $y$ are the compositions of the liquid and the vapor, respectively.

It is assumed that there is a total of $n_c$ components present in the whole system and no split of the liquid phase occurs for all possible compositions (homogeneous distillation). Further, the column to be modeled shall consist of $N_S$ separation stages. Feeds can enter the column on every stage $k$ with a specific pressure $p^k$ and a flow rate $F^k$ of which the fraction $q^{F^k}$ is liquid and $1 - q^{F^k}$ vapor. The liquid phase of the feed with composition $x^{F^k}$ and the vapor phase with composition $y^{F^k}$ are assumed to be in equilibrium. On every tray we have a vapor holdup $M^{V^k}$ with composition $y^k$ and a liquid holdup $M^{L^k}$ with composition $x^k$. Usually the first stage is referred to as condenser whereas stage $N_S$ (last stage) is referred to as reboiler. For these stages the different streams have to be specified according to design specifications for the column. E.g. for a total condenser the specifications $V^1 = 0$ and $U^1 = D$ hold.

Another set of equations which must be introduced are those referring to the vapor liquid equilibrium. For the sake of generality here the most general expression to describe these relations is used. It is depending on a partition coefficient $K^k_i$ describing the component distribution between the two phases.

$$y^k_i = K^k_i \left( p^k, T^k, x^k, y^k \right) x^k_i \quad (2.10)$$

The liquid phase and the vapor phase on each stage are assumed to be in equilibrium and so are the streams leaving the trays (liquid stream $L^k$ with composition $x^k$ and vapor stream $V^k$ at composition $y^k$). Assuming the pressure $p^k$ on the tray is known (e.g., constant in the column), the vapor-liquid equilibrium model gives $n_c$ linear independent equations.

In addition the next condition on the mole fraction must be fulfilled. It is a simple constraint which follows directly out of the definition of the mole fractions.

$$\sum_{i=1}^{n_c} x_i = \sum_{i=1}^{n_c} y_i = 1 \quad (2.11)$$

The last equations necessary to describe the system are the energy balances for every tray. It interconnects thermal behaviour with the distribution of the components.

$$\frac{d}{dt} \left( M^{L^k} H^{L^k} \right) + \frac{d}{dt} \left( M^{V^k} H^{V^k} \right) = L^{k-1} \Delta H^{L^{k-1}} + V^{k+1} \Delta H^{V^{k+1}} -$$

$$- (L^k + U^k) \Delta H^{L^k} - (V^k + W^k) \Delta H^{V^k} + F^k \Delta H^{F^k} \quad (2.12)$$

With the above equations the tray hydraulics are not yet considered. A relationship to determine the actual holdups on a tray would have to be introduced. Usually the
Francis correlation is used to specify the crest of liquid over the weir. This correlation needs information about the tray geometry though.

\[
h_{\text{crest}} = 750 \left( \frac{L_w}{\rho_w l_{\text{weir}}} \right) \tag{2.13}
\]

Where \(h_{\text{crest}}\) is the height of the crest in [mm], \(L_w\) liquid flow rate in \([\frac{\text{m}}{s}]\), \(\rho_w\) is the mass density and \(l_{\text{weir}}\) is the length of the weir in [m].

A further effect that is tightly knotted to tray geometry is the resistance to the vapor stream when passing the trays. Therefore an expression which would describe the pressure drop due to that and hydrostatic effects would still be needed. Alternatively the pressure \(p^k\) on the trays can be specified instead of dealing with an expression accounting for the effect mentioned before.

This set of equations is complete and describes the behaviour of a distillation column. Nevertheless they might be slightly too rigorous for many purposes, wherefore we will develop a simpler model in the next section, which allows for simpler handling and less computational effort while still providing a qualitatively correct description of a distillation column.

### 2.2.3 The Constant Molar Overflow Model

When approaching a problem it’s most often best to choose a model which is as simple as possible but as complex as necessary. The constant molar overflow (CMO) model derived in this section is a model which restricts itself to the two main phenomena in a distillation column: the vapor-liquid equilibrium and the material balances on every tray.

One of the first assumptions regarding the previous section is to neglect the energy balances. This simplification implies that there is no heat of mixing and that all components in the system have the same specific heats and the same molar heat of vaporization.

Moreover, very often it is a good approximation to assume ideal behaviour of the vapor phase. Thus the vapor liquid equilibrium reduces to the expression:

\[
y_i^k = y_i^k \left( x^k, p^k \right) \quad i = 1, \ldots, n_{c-1} \tag{2.14}
\]

There are other assumptions underlying the CMO model and they will be discussed now, since it’s crucial to know every assumption made when working with a model in order to understand which phenomena are considered and when the model is applicable or not.

Further simplifications regard the holdup on a stage. Noticing that the vapor holdup \(M_i^k\) is usually very small compared to the liquid holdup, it may be neglected.

Assuming (except for uppermost and lowest tray) that there are no side streams (denoted in the previous section as \(U\) and \(W\) in Equation 2.9) the following, simplified expression for the mass balances will be obtained.

\[
\frac{d}{dt} (M_i^k x_i^k) = L_i^{k-1} x_i^{k-1} + V_i^{k+1} y_i^{k+1} - L_i^k x_i^k - V_i^k y_i^k + q_i^F x_i^k + F_i^k \tag{2.15}
\]

\[
\quad i = 1, \ldots, n_{c-1}
\]
Furthermore if there is no feed on a particular stage, the corresponding terms will simply drop out of the equations.

At the very top tray, which corresponds to the condenser, there is slightly different situation. The streams $V^1$ and $L^0$ are zero since the condenser is at the very top of the column, not interacting with any other tray above. And the streams leaving this stage are either totally or partially condensed. Thus streams $W^1$ would be zero for a total condenser, whereas $W^1$ can have any other value for a partial condenser. One part of the material leaving the condenser is taken off as the distillate product $D = W^1 + U^1$ being either vapor or liquid or both. The rest (liquid) is refluxed to the tray. As that reflux $L^1$ is usually a manipulated stream, it is also denoted $L$, omitting the superscript in contrast to the streams $L^k$ inside the column. Thus the differential mass balance equations describing the condenser are:

\[
\frac{d}{dt} \left( M^1 x_i^1 \right) = V^2 y_i^2 - (L^1 + U^1) x_i^1 - W^1 y_i^1 + \left( 1 - q^{F^1} \right) F^1 y_i^{F^1} + q^{F^1} F^1 x_i^{F^1} \quad (2.16)
\]

\[
i = 1, \ldots, n_{c-1}
\]

In the case of a total condenser on the top stage, the composition of the reflux to the second stage is same as for the vapor entering the condenser, since there is no separation performed anymore in the condenser but the entering vapor stream is only condensed and then split up into two streams, the distillate product and the reflux. Therefore both of those two streams must have the same composition as the vapor stream entering the condenser.

\[
y_i^2 = x_i^1 \quad i = 1, \ldots, n_{c-1}
\]

\[
V^2 = D + L = W^1 + U^1 + L^1
\]

The bottom tray (reboiler) has to be treated separately as done before for the condenser. The liquid entering from above is collected and one part of the liquid is taken off as the bottom product $B = U^N$, the rest is boiled up again. The streams $L^N$ and $V^{N+1}$ are zero since there are no trays below the bottom tray with which it could interact and taking into account the above considerations the massbalances for the reboiler are:

\[
\frac{d}{dt} \left( M^N x_i^N \right) = L^{N-1} x_i^{N-1} - V^N y_i^N - U^N x_i^N + \left( 1 - q^{F^N} \right) F^N y_i^{F^N} + q^{F^N} F^N x_i^{F^N} \quad (2.17)
\]

\[
i = 1, \ldots, n_{c-1}
\]

In the Equation 2.17 it is assumed that the stream $W^N$ is zero, but obviously some of the bottom product could be taken as vapor and therefore this stream is not always zero.

Again the condition that the mole fractions must add up to unity must hold, since it follows directly from the definition of the mole fractions:

\[
\sum_{i=1 \ldots n_c} x_i^k = \sum_{i=1 \ldots n_c} y_i^k = 1, \quad k = 1 \ldots n \quad (2.18)
\]
All the equations derived until here from Equation 2.15 until Equation 2.18 can be rearranged and reduced by iterative insertion to form the global mass balance around the column which could also be derived directly:

\[
\sum_{k=1}^{n} \frac{d}{dt} M^k = \sum_{k=1}^{n} F^k - D - B \quad (2.19)
\]

Assuming that the holdup \( M^k \) on every tray remains constant, the derivatives reduce to:

\[
\frac{d}{dt} (M^k x^k_l) = M^k \frac{dx^k_l}{dt} \quad (2.20)
\]

and finally the total mass balances on every tray reduce to the simple relation \( \text{inflow} = \text{outflow} \).

A further simplification can be achieved by restriction to the special case that there is only one feed flow \( F \) to the column being fed liquid at its bubble point \( (q^{b^f} = 1) \) on stage \( f \). All flow rates can be calculated having specified two of them:

\[
B = F - D \\
V^k = L + D \quad k = 2, \ldots, N \\
L^k = L \quad k = 1, \ldots, f - 1 \\
L^k = L + F \quad k = f, \ldots, N - 1
\]

For the sake of simplicity and tradition \( U^N \) is denoted as \( B \) and \( U^1 + W^1 \) are taken together and denoted as \( D \). Finally \( L^1 \) is written as \( L \) only.

A further advantage of this restriction is that it leads to the conclusion that the mixtures will be at their boiling point on every tray. In order to draw that conclusion it must be bared in mind that at the beginning of this section the assumption of constant molar heats of vaporisation and negligible vapor holdup was made.

This model is complete enough to plug it into a suitable integrator and start working with it. However, first the simplifications and hidden assumptions must be clarified again and studied more precisely wherefore they will be treated again in the next section.

### 2.2.4 Simplifications in both Models

Again the importance of knowing the simplifications in the model above shall be emphasized. It is crucial for the understanding of a model, that the underlying assumptions are well known and deficient behaviour of a model under certain circumstances is known.

Thus, first of all, missing relations or underlying assumptions of both models shall be summarized here.

- It is assumed that all measures as flow rates, compositions, and holdups are given on the same basis, thus either molar or mass.
- The liquid phase as well as the vapor phase on all trays are perfectly mixed.
- The liquid and the vapor phase on the same stage are assumed to be in equilibrium.
- The pressure drop has to be specified.
To account for other measures expressions may be introduced to convert between them. Mainly because of physical relationships only available in other measures than molar ones the complexity of the column models is often increased and requires the introduction of those conversions. Therefore one will often have to calculate thermodynamic quantities in order to be able to make conversions of molar measures or mass to volumetric ones.

Imperfect mixing and vapor liquid equilibrium can be accounted for by introducing an efficiency expression. A commonly used efficiency expression for that purpose is the Murphree efficiency model which is defined for component $i$ on tray $k$ as follows:

$$E_i^k = \frac{y_i^k - y_i^{k+1}}{\tilde{y}_i^k - y_i^{k+1}}$$

(2.21)

where $\tilde{y}_i^k$ denotes the composition of the vapor which would be in equilibrium with the liquid composition $x_i^k$ on tray $k$. $y_i^k$ is the actual vapor composition on tray $k$. So, $y_i^k$ could be replaced in the mass balance equations by the following expression to account for the fact that equilibrium is not reached:

$$y_i^k = y_i^{k+1} + E_i^k (\tilde{y}_i^k - y_i^{k+1})$$

(2.22)

A pressure drop expression can be modeled if it is taken into account that the vapor rising in the column has to pass the liquid on the trays as well as the trays themselves. This causes a higher pressure towards the bottom of the column. However there are many different correlations to calculate those pressure drops. Nevertheless the most often used approach to account for the pressure drop is to impose a pressure profile to the column which accounts for the pressure drop. The pressure drop in that column profile is only estimated based on experience and common engineering knowledge as well on simple reference to static pressure drop due to the liquid height in the column.

2.2.5 Further Simplifications underlying the CMO Model

Further assumptions only underlying the CMO model and in addition to the ones mentioned in the section before are:

- The heat balances are neglected, thus it is assumed that there is no heat of mixing and that all components in the system have the same specific heats and the same molar vaporization enthalpies.
- The column shell is assumed to be adiabatic.
- The feed enters the column saturated, i.e. at it’s specific boiling temperature.

These assumptions have the consequence that on every stage in the column the amount of condensed vapor equals the amount of vaporized liquid

- The molar holdup on every stage is constant.

All those assumptions together explain the name of the model: "constant molar overflow" (CMO) model.

- The vapor holdups are neglected. In fact this can be justified as they would be significantly smaller than the liquid holdups. Also, by neglecting the vapour holdup on the stage, the calculation of the vapor-liquid equilibrium on the stages reduces from the calculation of an adiabatic flash to a bubble point calculation.
2.3 Packed Columns

Up to now only tray columns have been discussed. Nevertheless there are other possibilities. Instead of working with trays it is also possible to fill the column with a packing. The fluid would then flow down along the surface of the packing in a thin film which would allow for long and intense contact between the liquid and the vapor phase. Since the two phases are subject to a vapor liquid equilibrium they will be subject to subsequent change in concentration along the column and thus a separation will take place.

The advantages of packed columns are their compactness. They allow for significantly more stages per unit length than comparable tray columns. A further advantage which will be exploited in this project is the fact that the holdup in a packed column is mostly significantly smaller than in a corresponding tray column.

Now a model will shortly be sketched, whereby the emphasis is clearly on the conceptual side and thus details are omitted. The first equations to write are the mass balances. Instead of writing the mass balances for a tray as done for tray columns, here differential mass balances over the two phases must be written under the constraint that there cannot be any accumulation at the interface. We will consider a vapor stream $G$ with composition $y$ and a liquid stream with composition $x$:

\[
N = \frac{d (Gy)}{adz} = \frac{d (Lx)}{adz} = k_y' (y_i - y) = k_x' (x - x_i) \tag{2.23}
\]

The mass transfer $N$ for a component is equal to the change of that component in the vapor phase $\frac{d (Gy)}{adz}$ which must be equal to the change in the liquid phase $\frac{d (Lx)}{adz}$. Again those changes must be equal to the transport in both phases to the interface $k_y' (y_i - y)$ and $k_x' (x - x_i)$ respectively. Where $x_i$ and $y_i$ are the interfacial compositions, $k_x$ and $k_y$ are the mass transfer coefficients and $a$ is the area per unit volume available for mass transfer.

The vapor liquid equilibrium does not connect the bulk concentrations with each other this time, but the interfacial concentrations may now assumed to be at equilibrium.

\[
y_i^k = K (x_i, y_i, p, T_i) \tag{2.24}
\]

Assuming expressions for the mass transfer are available, examples may be found in Section 2.4.2, these material balances may now be integrated along the column to finally obtain the length needed for a certain separation task.

\[
Z = \int_0^Z dz = \int_0^{(Gy)} \frac{d (Gy)}{k_y' a (y_i - y)} = \int_0^{(Lx)} \frac{d (Lx)}{k_x' a (x - x_i)} \tag{2.25}
\]

It can be seen that those equations are already much more complex to solve than the corresponding ones in tray columns. Nevertheless their use is beyond controversy, since they are the only way to describe packed columns correctly. Furthermore the rate based approach to describe mass transfer allows the bulk concentrations in the liquid and in the vapor not to be in equilibrium and therefore provides a powerful tool to describe reality.
2.4 ASPEN Column Models

2.4.1 ASPEN RadFrac

In the previous sections a detailed and a simplified model have been presented to describe distillation column. The CMO model is the main model used in dynamic analysis and for bifurcations. It allows fast simulations without serious convergence problems of the algorithm. However, the behaviour observed has been validated with ASPEN RadFrac, a model provided by ASPEN Plus.

ASPEN RadFrac corresponds to the detailed column model developed in Section 2.2.2. Therefore it is very rigorous and according to the manual it’s suitable for all types of multistage vapor liquid fractionation operations. Especially due to the possibilities provided through ASPEN Dynamics a dynamic simulation suite, this model provided the possibility to perform detailed dynamic simulations.

The only limitation in ASPEN RadFrac is that it is actually an equilibrium based model and can account for non-equilibrium operations only through efficiency specifications. However, since in reality reaching the equilibrium during a process is not feasible, the results obtained with ASPEN RadFrac have to be validated and efficiencies have to be worked out. This is done with ASPEN RateFrac.

2.4.2 ASPEN RateFrac

RateFrac is an exchange rate base model and can be understood as a sophisticated implementation of the packed column model described in a previous section. Due to the fact that RateFrac is not an equilibrium model it must solve many more equations than the other models presented so far. So computing times are greater and also the convergence behaviour becomes worse, which has an even bigger impact on the applicability of the model.

RateFrac uses well-known and accepted correlations to calculate binary mass transfer coefficients for the vapor and the liquid phase as well as interfacial areas. The same is true for the heat transfer coefficients. Since there are different correlations which may be used for the transfer coefficients in columns according the possible internal layouts of the column (different kinds of packings and trays) only the ones actually used in our simulations will be stated here. The column considered and modeled is a packed column. While the mass transfer coefficients and the interfacial area available for mass transfer are calculated using the correlations developed by (Onda, Takeuchi and Okumoto 1968), they are brought together through rigorous multicomponent mass transfer theory (Krishna, and Standard 1976). RateFrac uses binary mass transfer coefficients to evaluate multicomponent binary mass transfer coefficients and component mass transfer rates between vapor and liquid phases.

The correlation for the mass transfer coefficient $k_{in}^L$ for the binary pair $i$ and $n$ in the liquid phase is

$$
\left[ k_{in}^L \left( \frac{\rho_L}{g \mu_L} \right)^\gamma \right] = 0.0051 \left( \frac{L}{a_\omega \mu_L} \right)^{\delta} \left( Sc_{in}^L \right)^{-\eta} (a_p a_p)^{0.4}
$$

(2.26)

where $\rho_L$ is the density of the liquid, $g$ the acceleration due to gravity and $\mu_L$ the liquid viscosity. $L$ is the liquid superficial mass velocity $\left[ \frac{kg}{m s} \right]$. While $a_p$ is the specific surface area of the packing, $a_\omega$ is the wetted interfacial area. The Schmidt number for
the binary pair \( i \) and \( n \) in the liquid phase is defined as:

\[
Se_{in}^L = \frac{\mu_L}{\rho_L D_{in}^L} \tag{2.27}
\]

where \( D_{in}^L \) is the binary Maxwell-Stefan diffusion coefficient for the binary pair \( i \) and \( n \).

On the other hand the correlation for the mass transfer coefficient \( k_{in}^G \) for the binary pair \( i \) and \( n \) in the gas phase is:

\[
\left( k_{in}^G \left( \frac{RT^G}{a_p D_{in}^G} \right) \right) = 5.23 \left( \frac{G}{a_p \rho_G} \right)^{0.7} \left( Se_{in}^G \right)^{1.5} (a_p d_p)^{-2} \tag{2.28}
\]

where \( d_p \) is the nominal diameter of the packing or the packing size, \( R \) the Universal gas constant and \( T^G \) the gas temperature. \( G \) is corresponding to \( L \) and is therefore the superficial mass velocity for the gas. Again the Schmidt number is defined as above, except that here in the gas case the properties for the gas have to be applied. The interfacial area available for mass transfer, thus the wetted interfacial area is given by the correlation:

\[
a_w = a_p \left\{ 1 - \exp \left[ -1.45 Re_L^{0.1} Fr_L^{-0.05} We_L^{0.2} \left( \frac{\sigma}{\sigma_c} \right)^{-0.75} \right] \right\} \tag{2.29}
\]

where \( \sigma \) is the surface tension and \( \sigma_c \) is the critical surface tension of the packing material. The characteristic, dimensionless numbers are defined as:

\[
Re_L = \frac{L}{a_p \mu_L} \tag{2.30}
\]

\[
Fr_L = \frac{a_p L^2}{g \rho_L} \tag{2.31}
\]

\[
We_L = \frac{L^2}{a_p \sigma \rho_L} \tag{2.32}
\]

The vapor phase and liquid phase heat transfer coefficients are calculated using the Chilton-Colburn analogy (King 1980). These analogy relates heat transfer coefficients with mass transfer coefficients, the Schmidt number and the Prandl number. The average heat transfer coefficient is therefore given by:

\[
h_{lc} = \frac{L}{a_{av}} Se_{in}^G e_{p,m} \tag{2.33}
\]

Generally speaking as it could been seen the transfer properties depend strongly on operating parameters such as flow rates and thermodynamic properties as densities, viscosities surface tensions and diffusion coefficients. But not only these quantities influence the behaviour. There are many more properties related to column geometry, which have big impact, i.e packing characteristics, tray geometry and layout.

The correlations used by RateFrac have been fitted to experimental measurements from laboratory and pilot plant absorption and distillation columns and therefore should be reliable. However the awareness should never be lost that they are correlations, which have been regressed and carry a certain error. They provide the possibility to observe tendencies, but cannot be used as final criterion for a layout. It should always be accounted for some unexpected behaviour through some spares in the design.
2.5 Column Profiles and Residue Curves

In Section 2.1.2, residue curves were derived from the detailed analysis of a simple batch distillation, thus as an analysis tool for such processes. Now it is shown how those diagrams can be used as a tool for analysis of distillation columns at steady state. Generally speaking the equations describing the effects governing a distillation column are complex and their solution requires a significant computational effort. Therefore it would be nice to have a simple tool which could predict column behaviour and also internal column profiles, such that, at an early stage of the design process, decisions about the feasibility of the separation with a real column could be made.

In this section the relation between column profiles and residue curves as well its use will be shown. This will only be done on a qualitative level and for a detailed derivation of the connections the reader is referred to specific literature.

2.5.1 Distillation Lines

Under the assumption of infinite reflux the column models derived before simplify significantly and especially the material balance equations in those models, since effects due to holdup and feed streams may be neglected. Based on this finding an approximation of the column profile may easily be deduced using only thermodynamic vapor liquid equilibrium data as it will be shown here.

Assuming infinite reflux the change in composition in the column due to any finite external flow is negligible. Therefore the liquid flowing from one tray to the tray below must have the same composition as the vapor coming upwards, while at the meantime the stage is still in equilibrium. As a consequence the following tray by tray difference equation may be derived for a distillation column:

\[
\begin{align*}
y^k &= y^k (x^k, p^k) & k = 1 \ldots n_{c-1} \\
y^{k+1} &= x^k & k = 1 \ldots n_{c-1}
\end{align*}
\]

(2.34) (2.35)

If those two equations are solved at constant pressure, they determine the so-called distillation lines. Distillation lines have been shown to be a valid expression for the column profile at infinite reflux. However when coming to real column profiles the assumption of infinite reflux does not hold anymore. Nevertheless, these equations have been shown to be a good estimate for the internal column profiles even at finite reflux, if the external flows, thus bottom, distillate and feed are small compared to the internal flows. Similarly as for residue curve maps distillation line maps may be defined. However they are not as easy to determine as residue curve maps and thus are not that widely used.

2.5.2 Residue Curves and Distillation Lines

In the previous section we saw that distillation lines are a good approximation for tray column profiles under certain conditions. In this section now it will be shown how residue curves actually are interconnected with distillation lines.

In the derivation of distillation lines the starting point is a discretized system and thus difference equations are used. In (Van Dongen and Doherty 1985) these equations (2.34, 2.35) are approximated with differential equations. The difference between profiles obtained with the differential equations and the distillation lines could be proved
to be very small. Moreover it is shown that at infinite reflux the differential equations correspond to the residue curve equations. As a consequence the profiles of tray distillation columns operating at infinite reflux are represented very good by a part of a residue curve.

Everything described so far concerns the description of tray columns, but there has also work been done starting from packed columns. With some simplifying assumptions regarding mass transfer (Laroche, Bekiaris, Andersen and Morari 1992) derived that the differential equations describing packed columns become identical to the residue curve equations at infinite reflux. As a result, ignoring the simplifications made, one could claim an exact coincidence between the column profile in packed columns and a section of a residue curve.

2.5.3 Conclusion

With the detailed models for distillation columns presented in the previous sections precise column profiles can be calculated. The disadvantage of these models is however, that a lot of information regarding the column is required to perform the calculations. In addition sophisticated software tools are necessary to solve the complex systems of equations describing the columns.

Here it has been shown, how column profiles can be approximated easily. Applying a few assumptions, in particular high reflux, the column profile of a tray or packed distillation column coincide with a part of a residue curve. These can be calculated using only thermodynamic data of the mixture involved and therefore can be determined a priori, which is a big advantage.

Using the residue curve maps to analyze a system a lot more of information can be obtained. In the next section it will be shown, how effects like multiple steady states and limit cycle behaviour can be predicted.

Finally, it is worth to remember that there is no tool which could describe column profiles exactly for any relevant case, there will always some assumptions be necessary. Nevertheless the approaches described above provide a good approximation of the behaviour in distillation columns and thus are a powerful tool to investigate them. It should never be forgotten that those tools rely upon assumptions and thus results obtained with those tools should be taken with care. On the other hand they give us the possibility for a fast and effective screening of the possibilities with separation through distillation. Some of the concepts introduced in the next sections will actually rely on this tool and its importance is not to be underestimated.
Chapter 3

Limit Cycle Behaviour in Distillation Columns

Now that an introduction into the area of distillation columns has been provided, this chapter shall give some background information about limit cycles in distillation columns and other heavily non linear behaviour.

First a tool is introduced to analyze different mixtures whereupon it is applied to give a short overview over multiple steady states in homogeneous azeotropic distillation. This is done since this topic is tightly knotted to limit cycle behaviour which will be described thereafter. This overview is kept short and focused to the basic knowledge necessary for the analysis of limit cycle behaviour in distillation. For further information regarding those phenomena the reader is therefore referred to (Dorn 2000) where also a detailed introduction into the area of bifurcation theory is given.

3.1 \(\infty/\infty\)-Analysis and Multiple Steady States in Homogeneous Azeotropic Distillation

In this section a tool, the so-called \(\infty/\infty\)-analysis, which allows to investigate qualitatively the existence of multiple steady states will be introduced. In Section 2.5 it has been shown that at infinite reflux the internal column profile will coincide approximately with a residue curve. This means that for a specific distillation column the distillate and the bottom composition have to lie on the same residue curve. Additionally there is another restriction to the composition of the bottom and the distillate flow rate: they must lie on the same straight line with the feed composition, in order to fulfill the global mass balance around the column.

The \(\infty/\infty\)-analysis assumes additionally to the infinite reflux also an infinite number of stages. From those two assumptions its name is derived. However an infinite number of stages is possible only if the column profile contains at least one pinch point. This may be explained with the fact that with every stage further separation is obtained, which cannot continue for ever. At the pinch points the driving force for separation given by the VLE tends to vanish (\(y\) approaches \(x\)) and thus the infinite number is "consumed" to reach perfect equality of the composition in both phases. Possible pinch points are the singular points of a residue curve diagrams, therefore all pure components and azeotropes.
Summarizing there are three conditions that must be satisfied for a column at infinite reflux and with infinite number of stages in order to be feasible:

- The column profile must coincide with a residue curve, therefore the distillate and the bottom composition must lie on the same residue curve.
- The column profile must contain at least one pinch point.
- Distillate, bottom and feed composition must lie on the same straight line.

Based on these three conditions a product path in dependence of the distillate flow rate $D$ can be sketched. Hence this will be presented for a mixture of the 001 class according the systematic nomenclature of (Matsuyama and Nishimura 1977) in the next section. During that example bifurcation behaviour will be shown and the existence of multiple steady states may be observed.

### 3.1.1 $\infty/\infty$-Analysis – Case Study

As stated in the previous section, here an $\infty/\infty$-analysis will be performed. During this analysis, the distillate flow rate $D$ is varied from zero to the feed flow rate $F$.

If the distillate flow rate $D$ is zero the composition of the bottom must equal the feed composition. Considering the restrictions introduced above, the distillate must be at the unstable node, in this case the azeotrope.

![Figure 3.1: Qualitative sketch of an $\infty/\infty$-analysis, where $Az$ indicates the azeotrope composition, $F$ the feed composition and $L$, $I$ and $H$ the light, intermediate and heavy components respectively.](image)

Rising the distillate flow rate the bottom composition will move away from the feed, while the distillate remains at the azeotrope. This will go on until the bottom hits the boundary of the composition space. Then the bottom composition follows the boundary, until it reaches the stable node, which is the pure heavy component. After the bottom hit the boundary, the distillate starts to move away from the pure azeotrope composition and its location may be determined with the three rules introduced before in Section 3.1. A qualitative sketch of the whole analysis is found in Figure 3.1.

If it is now looked at the bottom composition during this whole process and the fraction of heavy component in the bottom product is plotted versus the distillate flow rate, a graph similar to the one depicted in Figure 3.2 is obtained. Looking carefully at this graph it can be noticed that within a certain range, there are several possible
solutions for one value of our operating parameter, the distillate flow rate $D$. There is an output multiplicity in dependence of $D$ and two fold bifurcations at the turning points of the graph in Figure 3.2 cause the existence of multiple solutions.

![Figure 3.2: Qualitative bifurcation diagram, where the mole fraction of the heavy component is plotted versus the distillate flow rate.](image)

### 3.1.2 Prediction of Multiplicities

In the previous example, the detection of the fold bifurcations was done visually, just looking at the turning points in the graph. However they could be detected directly from the residue curve diagram, if the geometric condition for multiple steady states is reformulated as proposed in (Bekiaris, Meski, Radu and Morari 1993). In Figure 3.3 a part of the distillate and the bottom product path are shown. This picture was taken from (Dorn 2000).

If an equilibrium is considered with the corresponding profile and product composition $x^D(2)$, $x^B(2)$, a condition for a generic fold bifurcation to occur at that equilibrium is that the tangent vectors to the product paths in $x^D(2)$ and $x^B(2)$ are in an angle of 180 degrees. For nondegeneracy of the fold bifurcation, the angle between the two tangent vectors must not have a maximum or minimum in the bifurcation point.

![Figure 3.3: Geometric condition for the detection of fold bifurcations in the product path.](image)
3.1.3 \( \omega \)-Region

Analogous as for the geometric condition for fold bifurcations a region may be defined wherein the angle between the tangent vectors of the same residue curve is more than 180 degrees. This implies an non monotonous evolution in the composition of all three components along the residue curve. This region was referred to as \( \omega \)-region by (Dorn 2000).

A different definition for the \( \omega \)-region, which leads to the same solution, can be made upon the concepts of the \( \infty/\infty \)-analysis. It can be defined as the subspace of possible distillate compositions for columns with infinite number of stages at infinite reflux, showing a non monotonous profiles in all concentration profiles.

The \( \omega \)-region is not related directly to the existence of multiple steady states, but rather to the existence of limit cycle behaviour which will be discussed in a later section. However its definition is provided here, since it is closely related to the requirements for nondegeneracy of fold bifurcations.

3.1.4 Validation of Multiplicities

The concepts mentioned in the sections before are described in more detail in (Bekiaris et al. 1993) and in (Bekiaris and Morari 1996). Moreover the existence of multiple steady states has also been validated through simulations and experiments (Güttinger, Dorn and Morari 1997). It has also been shown through numerical and qualitative analysis that the intermediate branch corresponds to unstable steady states, while the lower branch corresponds to stable steady states and the higher branch to both, stable and unstable steady states. For further information regarding multiple steady states it is referred to the publications cited before and to (Dorn 2000).

The main interest of this work are not bifurcations themselves, but limit cycle behaviour and thus bifurcations which allow for sustained oscillations and limit cycles. The kind of bifurcations which actually allows for limit cycle behaviour will therefore be discussed in the next section.

3.2 Limit Cycle Behaviour in Homogeneous Azeotropic Distillation

As it has been shown, some bifurcations may be detected geometrically, such as fold bifurcations (turning points). However the interest of this work is focused on limit cycle and consequently on a different kind of bifurcations.

Bifurcations which allow limit cycle behaviour to occur are Hopf bifurcations. Hopf bifurcations occur at points where there is a local exchange of the equilibria, thus at points where a transition of eigenvalues from the negative half plane to the positive half plane occurs and the steady state solution changes from stable to unstable or the other way around. Such an exchange of stability does not only occur at Hopf bifurcations, but as well at turning points, which is based on the fact that of the two branches of equilibria approaching a turning point one or both can be unstable but it is not possible that both are stable. However, to have a Hopf bifurcation, a change of the stability of the equilibria at a point which is not a turning point is needed.

There are two kinds of Hopf bifurcations: supercritical and subcritical. The supercritical type results in a stable limit cycle surrounding an unstable stable steady state, while the subcritical results in an unstable limit cycle surrounding a stable steady state.
It can be shown through numerical analysis that in the upper branch of the bifurcation diagram shown in Figure 3.2 there occurs a change of stability of the equilibria twice, and thus there must be Hopf bifurcations. These Hopf bifurcations have been shown to be supercritical. Up to now subcritical Hopf bifurcations have never been observed in distillation columns (to the authors knowledge).

The change of stability described above can be traced back to the fact that a requirement must be fulfilled in order that sustained oscillations may occur. To have limit cycle behaviour in a distillation column there must exist an $\Omega$-region in the residue curve diagram and the distillate composition has to lie within this region. This requirement was illustrated in (Dorn 2000) quite in detail. Here we will restrict ourselves on the definition of this requirement, since it will only be used as a qualitative approach to find systems which could evolve limit cycle behaviour.

### 3.2.1 Validation

The existence of Hopf bifurcations and limit cycle behaviour has been validated in (Lee, Dorn, Meski and Morari 1999) through both, a CMO model and a sophisticated equilibrium stage based model, ASPEN RadFrac. This validation was performed through dynamic simulation as well as through analysis of the bifurcations occurring in the product paths. However the existence of sustained limit cycle behaviour has never been validated experimentally. The preparation of this validation is the aim of this work.

In order to prepare this validation the dynamic behaviour has to be investigated and an experimental set-up has to be worked out. This will be done in this work first by looking at the results retrieved by (Dorn 2000) and then additional investigations on aspects of the dynamic behaviour will follow.

### 3.2.2 Oscillations

Because it is closely related to the limit cycle behaviour discussed in the previous section and its big importance for technical processes the occurrence of simple, underdamped oscillations will be mentioned here as well. This oscillating behaviour may occur without the existence of limit cycle behaviour and the oscillations show an underdamped character in the open loop response.

Oscillations arise, when the two governing eigenvalues (the ones with the greatest real parts) of the system are actually a pair of complex conjugates. So if the system which is at that steady state with stable character, is perturbed it will exhibit underdamped oscillations when approaching the steady state again. These effects will hold in the neighborhood on both sides of a Hopf bifurcation point, where a stable focus exchanges stability. In the following a region on a steady state branch corresponding to foci will be called an oscillation region only. According to the theory of bifurcation, the change from a node to a focus is not a bifurcation.

This background regarding the characteristics of bifurcation and the prediction of limit cycles suffices for the purpose to provide some insight into this work and thus it will be switched to a much more practical aspect. Since it is the aim of the project to measure limit cycle behaviour, the approaches which may be used for measurement will be presented in the next section. After that, a sketch of the starting point of this project will be provided through a case study, whereafter the investigations performed will be discussed in detail.
3.2.3 Measurements of Limit Cycles

When measuring limit cycles in distillation columns the same requirements must hold as anytime when sustained oscillations are to be measured. Oscillations show two characteristic properties, which are the amplitude of oscillation on one hand and the period of oscillation on the other hand. These two quantities are illustrated in Figure 3.4.

![Illustration of amplitude and period of oscillation, the two significant quantities when measuring oscillations](Figure 3.4)

In order to have measurable limit cycle behaviour first of all the amplitude has to be big enough such that it may be detected by the measurement equipment, i.e. it must be significantly bigger than random noise generated by the measurement and the experimental setup. Secondly the period of oscillation must fit into the time scale of our measurements. It must not be too small, such that the resolution of our measurements cannot distinguish between single cycles on one hand, and it must not be too big. If the period of oscillation is too big the duration of an experiment is far too long and constancy in operation becomes more and more difficult to maintain. Constancy in operation is very crucial though since fluctuations in the operating conditions might introduce oscillations themselves and thus might make the results of experiment worthless.

Measuring the amplitude of oscillation will however not be the problem in the case of homogeneous azeotropic distillation. It has been shown (Dorn 2000) that in homogeneous azeotropic distillation fronts are present in the distillation column. These fronts are most often referred to as temperature fronts, since there is a sharp change in temperature over a relatively short range. This change in temperature is correlated with a sharp change in concentrations as well. While for the temperature a front can be observed this is not always true for the compositions. The composition profiles show either fronts or peaks.

When the column starts to oscillate, the front will start to move up and down the column. Because of its characteristic sharp change in properties this introduces a significant change in temperature and composition at a point where this front passes by. Thus if a measurement is performed in the column in the range of the temperature front, the amplitude of oscillation should definitely be big enough to be measured. The behaviour of the temperature front in the column and its shape are sketched qualitatively in Figure 3.5
The period of oscillation has been shown to be the critical measure in homogeneous azeotropic distillation. In first simulations (Lee et al. 1999) the period of oscillation has been found to be too long for experimental purposes. The period of oscillation is so long that stable operating conditions cannot be guaranteed anymore and the cost of the experiment would be very high, due to both technical equipment and running costs. This aspect is however discussed later on in detail. Investigations will be presented which aim to reduce the period of oscillations in order to make the measurements of limit cycle behavior in homogeneous distillation feasible.
In this chapter, first the ternary mixtures used in previous investigations will be presented. Each of those systems will be shortly discussed upon their characteristics and in special their $\Omega$-region.

After having introduced those systems, a case study will be performed to provide the reader with a first, detailed sketch of the procedure to apply when investigating limit cycle behaviour in homogeneous azeotropic oscillation. So the reader will be made familiar with the problems and characteristics of systems showing limit cycle behaviour. This approach shall prepare the reader for the discussions in the chapters afterwards.

4.1 Ternary Mixtures Subject to Investigations

In this section we will present the most important mixtures which have been subject to investigations in previous work. The underlying mixtures are probably the most important factor to our investigations, thus it is of major importance to know them and the according characteristics.

To present the mixtures the source of the thermodynamic data used will be presented and their reliability will be discussed, whereafter the characteristics of the mixture will be discussed based on a residue curve map. The residue curve maps where drawn using the ”MATLAB Toolbox for thermodynamic Calculations” developed at ETH Zürich (Metzler 1999).

When presenting the residue curve maps a special focus is set on the $\Omega$-region, since its size mainly determines the range of conditions which can lead to limit cycle behaviour. A necessary criterion for the existence of limit cycles is that the distillate composition must lie within the $\Omega$-region. Therefore within a large $\Omega$-region the operating parameters may be varied wider without losing limit cycle behaviour than in a small one.

4.1.1 Methanol - Methylbutyrate - Toluene

This mixture was subject to detailed investigations in (Dorn 2000). The residue curve map depicted in Figure 4.1 has been drawn using the Wilson property model for the activity coefficients and therefore the fugacities of the liquid phase. It is a mixture belonging to the class 001 according to the systematic naming of (Matsuyama and
There is only one azeotrope lying between toluene and methanol at about 88% (mole) methanol. This allows for quite a big \( \Omega \)-Region and quite a wide range for the operating parameters which would allow to have oscillations.

However, there are some uncertainties whether there could be additional azeotropes between methylbutyrate and methanol or toluene respectively. In (Gütinger et al. 1997) the thermodynamic properties for these two binary mixtures were reported to be estimated with UNIFAC with Dortmund corrections.

This uncertainty in the thermodynamic data is problematic and must be discussed with respect to an experimental validation of limit cycle behaviour. An additional azeotrope could influence the oscillations significantly and cause a decrease in the range of conditions wherein oscillations occur. This uncertainty regarding a second azeotrope arises mainly because of the fact that no experimental data concerning this mixture could be retrieved. Therefore experimental validation of the chemical property parameters should be considered.

Despite of these uncertainties and the lack of regressed thermodynamic data, it can be assumed that the estimated thermodynamic data is representing the actual behaviour quite closely, since during the experimental validation of multiple steady states in homogeneous azeotropic distillation exactly this mixture was used and the experimental results reproduced the predictions from simulations quite closely (Gütinger et al. 1997). Thus since in this work the same parameter sets will be used it can be concluded that the predictions based on those parameters should hold for the purpose of investigating that system. Also it can be concluded that there should be no azeotropes because of the similarity of the results between the experimental set-up and the simulation. The actual thermodynamic property coefficients can be retrieved in in the Appendix.

Figure 4.1: Residue curve map for the mixture Methanol - Methylbutyrate - Toluene.
CHAPTER 4. INITIAL STATUS QUO

4.1.2 Acetone - Benzene - n-Heptane

Also this mixture was subject to investigations in (Dorn 2000), however these were not as detailed as for the mixture of methanol - methylbutyrate - toluene described in Section 4.1.1. So there are some open questions regarding this mixture and its dynamic behaviour compared to the Mixture presented before. As it can be seen from the residue curve map in Figure 4.2 it is a mixture belonging to the class 001 according to the systematic naming of (Matsuyama and Nishimura 1977). Again the residue curve maps were drawn using the Wilson property model for determining the activity coefficients. The Wilson parameters used in this mixture originate from experimental data and thus are very reliable. The actual thermodynamic property coefficients can be retrieved in in the Appendix.

There is only one azeotrope lying between n-heptane and acetone at about 92% (mole) acetone. Thus the Ω-region is significantly smaller than the one reported for the mixture of methanol - methylbutyrate - toluene described in Section 4.1.1, but it is still big enough to allow for reasonable investigations and simulations.

![Aceton−Benzene−n−Heptan Residue Curve @ p=101325 Pa](image)

Figure 4.2: Residue curve map for the mixture Acetone - Benzene - n-Heptane.

However this mixture is only of scientific interest and cannot be used for experimental validation of limit cycles in homogeneous azeotropic distillation, since it contains benzene which is highly carcinogen and thus would be too dangerous and too harmful for an experimental set-up.

4.2 Case Study Showing Sustained Oscillations

In in (Dorn 2000) and in (Lee et al. 1999) a column set-up was presented that showed limit cycle behaviour in a detailed dynamic simulation. It was decided to take this set-up as a basis for further investigations and to verify personal expectations. The
set-up and model details are described in the next sections. There will also be a short comparison with the results published in (Lee et al. 1999) and some additional results will be presented in the coming sections.

### 4.2.1 Set-Up of Simulations

The system to be investigated is the mixture of methanol-methylbutyrate-toluene, which is the most interesting regarding an experimental set-up. As reported in (Lee et al. 1999) this mixture oscillates under the conditions listed in Table 4.1.

<table>
<thead>
<tr>
<th>Table 4.1: Column set-up as presented in literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N^\circ \text{ of trays (including condenser and reboiler)} )</td>
</tr>
<tr>
<td>feed tray (counting from condenser)</td>
</tr>
<tr>
<td>tray liquid holdup [kmol]</td>
</tr>
<tr>
<td>condenser liquid holdup [kmol]</td>
</tr>
<tr>
<td>reboiler liquid holdup [kmol]</td>
</tr>
<tr>
<td>column pressure [atm]</td>
</tr>
<tr>
<td>reflux flow rate [kmol/h]</td>
</tr>
<tr>
<td>feed flow rate [kmol/h]</td>
</tr>
<tr>
<td>feed composition methanol (mole fraction)</td>
</tr>
<tr>
<td>feed composition methylbutyrate (mole fraction)</td>
</tr>
<tr>
<td>feed composition toluene (mole fraction)</td>
</tr>
</tbody>
</table>

Looking at those specifications they seem to be complete and indeed they are for a simple model as the CMO model, which allows to specify the quantities in that way. However, since it was desired to investigate this set-up with ASPEN RadFrac in dynamic simulation with ASPEN Dynamics, some uncertainties arose. These uncertainties concerned the setup of the trays in the column as well as the reboiler and the condenser, since ASPEN requires geometrical specifications and thus volumetric ones, which cannot be translated easily to a specification of the holdup in terms of moles. Therefore decisions about the geometrical set-up of this equipment had to be made.

The equipment mentioned beforehand has been modeled according to the dimensions listed in Table 4.2. In order to model this equipment the density of the leaving streams was estimated with ASPEN PLUS and then the geometries have been chosen such that the dimensions would lead to a holdup as close as possible to the estimated one. However, this estimation is quite crude especially due to the fact that the specification of the trays is chosen to be uniform along the column although the density obviously is not. In the case of the trays the design is done for an arbitrary average density, the same is true for the vessels of reboiler and condenser.

This is now a complete set of parameters for the column set-up under ASPEN RadFrac. However another specification has to be made in order to be able to run an appropriate simulation. The specification mentioned is rather a decision: which property model to choose. This will be discussed in the next section.

### 4.2.2 Thermodynamic Properties

In (Lee et al. 1999) once the Wilson Model and once the UNIQUAC model are used for the simulations set-up as before. While the liquid activity coefficient is calculated
Table 4.2: Design decisions to specify set-up in ASPEN RadFrac

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column diameter [m]</td>
<td>2</td>
</tr>
<tr>
<td>Weir height [m]</td>
<td>0.07</td>
</tr>
<tr>
<td>Tray spacing [m]</td>
<td>0.6096</td>
</tr>
<tr>
<td>Condenser and reboiler</td>
<td></td>
</tr>
<tr>
<td>Vessel type (ends)</td>
<td>Flat</td>
</tr>
<tr>
<td>Length [m]</td>
<td>1</td>
</tr>
<tr>
<td>Diameter [m]</td>
<td>0.7</td>
</tr>
<tr>
<td>Distillate density [kmol/\text{m}^3]</td>
<td>21.13</td>
</tr>
<tr>
<td>Bottom density [kmol/\text{m}^3]</td>
<td>8.17</td>
</tr>
</tbody>
</table>

with one of the models mentioned before, the gas phase is assumed to behave ideally. Due to a slight uncertainty about which Wilson parameters are used and due to the fact that the UNIQUAC model is easily accessible in ASPEN it has been decided to run the simulations presented here with UNIQUAC. As a result of a lack of parameters for the UNIQUAC model some of the binary interaction parameters had to be estimated with the UNIFAC model without Dortmund corrections.

With the decision for the UNIQUAC model, everything which has to be decided for the simulation is specified and a dynamic simulation can be run in order to retrieve first results. The results and the comparison with the original results from (Lee et al. 1999) will be presented in the next section.

### 4.2.3 Results

Generally the oscillations are most intense in the region of the temperature front in a column because the temperature front tends to move during oscillations which implies a sharp change in the mixture composition and the temperature during oscillation, if the position of the measurement is fixed. Consequently in (Dorn 2000) the behaviour in the region of the temperature front is reported, which is allocated around tray 12. For illustration purposes the oscillations observed in this simulation are plotted in Figure 4.3 and according to the approach in (Dorn 2000) concentrations of the three components and the temperature on tray 12 are plotted against time.

The reflux needed to obtain limit cycle behaviour was found to be significantly different from the one reported in (Lee et al. 1999). As reported in (Dorn 2000), the region of limit cycle behaviour, has been found to be very sensitive to the vapor liquid equilibrium model and data. In the set-up presented here, the reflux to feed ratio is 12, whereas no limit cycle behaviour could be observed for a reflux to feed ratio of 20.

However, in (Lee et al. 1999) the according set-up using the Wilson property model is reported to run only at a reflux to feed ratio of 20, whereas no such behaviour could be found at a reflux to feed ratio of 12. Although a simulation using the UNIQUAC model model is reported in that publication as well, no information about the reflux needed is reported.
The period of oscillation reported in (Lee et al. 1999) is somewhere in between 100h and 150h depending on the thermodynamic properties and the model used. However in the simulations performed here this period of oscillation has been found to be around 75h only.

A possible explanation of this difference in the period of oscillation may be given by differences between the two set-ups, the one presented here, and the one presented in (Lee et al. 1999). First of all, it has already been stated in Section 4.2.1 that there is an uncertainty about the tray geometry to be used and the estimation of their holdup. Thus the holdup in the column presented here is very likely to be significantly different from the one used in (Lee et al. 1999). As we will see in a later section, holdup has a big impact on column dynamics and period of oscillation, and could therefore be a valid explanation.

On the other hand the choice of our property model was UNIQUAC, but some interaction parameters had to be estimated using UNIFAC. It could not be determined whether in the simulation in (Lee et al. 1999) actually parameters have been estimated or how they were retrieved, thus there might be a difference as well, which could explain the different reflux needed to obtain oscillations as well as the different periods of oscillations.

The effects due to thermodynamic data seem overweight to most other phenomena and are very important for the dynamics of the system. This would not be expected since both sets of parameters within their models predict very similar behaviour for the vapor liquid equilibria. Due to these uncertainties absolute values retrieved with simulation must be taken with care and qualitative results should be weighted far more than quantitative one. Furthermore it will be shown in this work that though it must be taken into account that the thermodynamic model used highly influences the outcome of a simulation, there are other possibilities to influence the system and to compensate for slight changes introduced by different thermodynamic behaviour.
4.2.4 Period of Oscillation – Conclusion

The limit cycles found with the simulation mentioned in the previous section showed a period of oscillations of about 75 hours. This period of oscillation is far too long for any experimental validation. For an experimental validation at least 3 full cycles have to be measured, which does not yet include the start up of the experimental set-up. Baring in mind complications which might arise the first few times a set-up is tried. Thus such a time is completely unrealistic and it must be tried to shorten it.

There are two approaches to reduce this time, the first one would be to look for a suitable system, which would have shorter periods straight away, while on the other hand, the experimental set-up may be changed and design options may be used to reduce this period of oscillations. In the next chapter the search for systems, which would be suitable for an experimental set-up and its outcome will be sketched, whereupon an analysis of the dependence of the period of oscillation upon the experimental set-up is presented.
Chapter 5

Search for a Different Mixtures

The ternary systems observed in Chapter 4, have a period of oscillation which is far too long for reasonable experimental measurements. One of the first ideas when observing this, is obviously to look for a new system, which would have a lower intrinsic period of oscillation.

This was done systematically and the proceeding as well as the criteria used for that search will be presented here. First the requirements for a new system will be defined and then the screening procedure will be sketched. Afterwards the results of that search will be presented.

For the presentation of the results the according residue curve maps were drawn using the "MATLAB Toolbox for thermodynamic Calculations" (Metzler 1999). Furthermore some characteristic properties of the ternary systems found will be presented.

5.1 Criteria for a new System

First of all the criteria for the search of a new ternary system shall be defined here, whereupon in the next section a systematic proceeding to search for such a system is proposed, which will be based on these requirements.

5.1.1 Chemical Reactions

The interest of this work is homogeneous azeotropic distillation and thus it is of major importance that the components in the ternary system would not react with each other. This includes not only chemical reactions in classical terms but as well acid base interactions which could evolve unpredictable influences on the system.

However this feature is hard to check in advance, since during a systematic screening it would take too much effort to check all possible combinations for reactions. Therefore this will only be checked after having found a ternary mixture that shows interesting properties with respect to limit cycles.

5.1.2 Harmless Components

The goal of this work is to prepare an experimental set-up, therefore it is looked for a mixture which can actually be used in an experimental set-up. Such a mixture should not have dangerous properties, since that would imply an experiment to be carried out
under special security equipment or might even have the consequence that an experiment is not even allowed to be carried out.

Therefore components which are extremely toxic are not taken into account for screening right away. The same is true for components are extremely dangerous in terms of flammability or which even show the tendency for explosions. The last two points are of major importance since distillation is a thermal process, where big amounts of energy are needed for heating and operation in general. Thus there are always hot spots in the actual set-up where those components could catch fire or even cause an explosion.

5.1.3 Ease of Separation

A rather technical issue is the separability of the mixture. When looking at distillation, the relative volatility is quite a good measure for the separability of a mixture. This relative volatility should be significantly different from unity in order to have an easy to separate mixture.

An easily separable mixture would be favorable for the experimental set-up, since in this special case of azeotropic distillation it is necessary to get quite close to singular points in the residue curve diagram, where the driving force for separation is small anyway. Therefore quite a big number of stages are needed to get there. If the relative volatility would be close to unity it would become even more difficult and the number of stages needed to accomplish the separation task would become significantly bigger. More stages imply a bigger column, which can be a problem since the size for a column in an experimental set-up is actually restricted by the laboratory facilities. As a consequence the mixture should be as easy to separate as possible in order to have a column which is as small as possible.

5.1.4 Big $\Omega$-Region

In Section 3.1.3 the concept of the $\Omega$-region was introduced. It was also stated that the distillate composition would have to lie within this region in order that limit cycle behaviour is possible.

If the $\Omega$-region is big this generally implies that once the distillate composition is in that region there is quite a big range wherein the operating parameters or the design may be varied until the distillate composition would drop out of that region. Later in this work the dependence of the period of oscillation upon different parameters and design decisions is investigated and quite some influences will be found. Thus to be able to exploit these influences it would be favorable to have a big $\Omega$-region wherein it can be played with those parameters.

Another reason which makes a big $\Omega$-region favorable is the fact that models only describe reality, and in fact the real behaviour might differ from the simulated one. In the case of a big $\Omega$-region it would then be easier to find operating conditions which would allow for limit cycle behaviour although the uncertainty. Therefore a big $\Omega$-region implies a bigger tolerance for differences between the actual set-up and simulations.

5.1.5 Simplicity of the Residue Curve Map

In order to be able to make theoretical predictions the system should have a simple residue curve map. Therefore it is tried to maintain a comparable structure to the
two systems presented in Sections 4.1.1 and 4.1.2. Preferably it is looked for systems belonging to the classes 001, 003, 103, 130, 201 and 401 according to the systematic naming of (Matsuyama and Nishimura 1977), thus a systems with only one or two azeotropes and maximally two distillation regions.

5.1.6 Homogeneity

The interest of this work is homogeneous azeotropic distillation and thus the resulting system should allow for mixing throughout the whole composition space. However as for chemical reactions, this feature is hard to check in advance, since during a systematic screening it would take too much effort to check all possible combinations for heterogeneity. Therefore this will only be checked after having found a ternary mixture that shows interesting properties with respect to limit cycles.

5.2 Systematic Approach of Search

Now that the requirements for a new system are defined a systematic approach for the screening shall be developed based on the assumption that a database with a certain number of components is available.

When looking at the requirements for single components defined in Section 5.1, some components could be sorted out right away. These components are the ones which either showed highly toxic properties (such as benzene) or highly dangerous behaviour regarding flammability and explosions.

An important requirement which was defined in the previous section was the one of a big $\Omega$-region. When looking at this requirement a little bit closer it can be seen that a big $\Omega$-region implies in most cases a binary azeotrope close to equimolarity. This could therefore be a first criterion for searching.

As a second step a third component could be sought in order that the system would become one of the ones stated above. The limiting case for a binary azeotrope to be considered was set to composition of at least 12% (mole) in either component, which corresponds to the value for the mixture methanol-methylbutyrate-toluene presented in Section 4.1.1. Then it can be tried to find an suitable entrainer, such that the ternary system obtained belongs to one of the classes stated in Section 5.1.

Finally, when a system is found based upon the proceeding stated before, it is checked for the other requirements presented in the previous sections, which rely on the interaction between the components. Therefore the relative volatilities must be checked in order to verify that the system is easily separable. Finally the components must not undergo chemical reactions with each other or form inhomogeneities.

5.3 The Screening

With this systematic approach a database of about 50 components has been screened. After the screening of this database, only one ternary mixture out of those 50 components corresponds to a system with a big $\Omega$-region. Unfortunately this system does not fulfill the criterion for easy separability and cannot be used for further investigations.

As a result of this screening the decision made is to proceed all the investigations with the focus on the mixture which has been used already before: methanol-methylbutyrate-toluene. It is the system which better fulfills the requirements made
before. This mixture will be used in all further considerations. Despite of this clear focus most findings will also be checked with the system acetone-benzene-heptane, in order to validate the applicability to other systems.

But before starting with these investigations, there will be a short presentation of two systems. The first one is the only system which has been found to show a big $\Omega$-region. The second one is just an additional system, which shows an interesting residue curve map but is not investigated further because of the awkward properties of one of its components, i.e. formic acid which is very corrosive.

### 5.4 Ethanol-Triethylamine-Butylethylether

The only system, which has been found to fulfill the criterion of a big $\Omega$-region, is the mixture of ethanol-triethylamine-butylethylester. This system has an azeotrope between ethanol and butylethylester at about 65\% (mole) ethanol and an azeotrope between ethanol and triethylamine at about 90\% ethanol. Therefore the system belongs to the class 201. The residue curve map for this mixture is shown in Figure 5.1. As it can be seen the $\Omega$-region for that mixture is very big compared to the other two systems described before in Sections 4.1.1 and 4.1.2 and therefore it is very promising.

![Residue curve map for the mixture ethanol-triethylamine-butylethylether](image)

**Figure 5.1: Residue curve map for the mixture ethanol-triethylamin-butylethylether**

Unfortunately hardly any experimental data was available for this system and regressed properties could only be retrieved for the binary mixture of ethanol and triethylamine. All other parameters had to be estimated using UNIFAC. The uncertainty regarding the behaviour of this mixture is quite big and it should be validated experimentally if further investigations are considered.

However this uncertainty is of minor importance for this work, since this mixture is not be considered for further investigations. The reason is that relative volatilities for this mixture are very close to unity and thus a separation through distillation becomes
very hard. An experimental set-up would be far too big in order to be realized. Therefore this mixture cannot be used for the purposes of this work.

A further aspect which might be unfavorable regarding this mixture is that it actually contains an ether which can be quite sensitive to heat because ethers tend to form peroxides if they are exposed to air. Peroxides are critical since they could cause explosions.

### 5.5 Formic Acid-Isobutanol-Pyridine

During the investigation of different mixtures an interesting residue curve diagram was found for the mixture of formic acid-isobutanol-pyridine. Formic acid is very corrosive and tends to form dimers which makes the operation of distillation columns with formic acid a very hard task and thus is not suitable to validate a very sensitive behaviour as limit cycles are. Nevertheless the residue curve map shall be depicted in Figure 5.2. As we can see this mixture belongs to the class 130 according to the systematic nomenclature of (Matsuyama and Nishimura 1977).

![Formic Acid – Isobutanol – Pyridine Residue Curve @ p=101325 Pa](image)

**Figure 5.2:** Residue curve map for the mixture formic acid-isobutanol-pyridine

The only stable node of that system is the high boiling azeotrope between pyridine and formic acid, therefore between the intermediate and the heavy component, while the only unstable node is the low boiling azeotrope between isobutanol and pyridine. The interesting thing about this mixture is, that it belongs to a completely different class than all other systems presented up to now. Therefore this system might be valuable to investigate effects due to changes of the system, although it cannot be used for experimental purposes.
Chapter 6

Qualitative Effects on Limit Cycle Behaviour

In this chapter qualitative predictions shall be made regarding the dependence of limit cycle behaviour upon the two key parameters feed composition and reflux flow rate. This qualitative depiction is based on work presented in (Dorn 2000).

First the effects introduced by changing the feed composition will be discussed. Afterwards the slightly more complicated case of reflux will be presented, focusing on the connections with the feed composition. The results presented in this chapter consider systems of class 001, but can be extended to other systems as well.

6.1 Influence of Feed Composition

The feed composition is a parameter which can be easily varied within an experimental setup. However the range wherein the feed composition may be varied in order to maintain oscillations is restricted due to the fact that the bifurcation requirements have to be fulfilled in order to have the possibility of limit cycles.

First of all it is important to understand how the feed compositions may be varied. Here a ternary mixture is considered. Baring in mind the physical restriction that the mole fractions must add up to unity, the system may be parameterized in order to reduce the number of variables. The following two ratios are defined:

\[
x_{LI} = \frac{x_L}{x_I}
\]

(6.1)

\[
x_{LH} = \frac{x_L}{x_H}
\]

(6.2)

Where \(x_L, x_I\) and \(x_H\) are the mole fractions of the light, intermediate and heavy component. Defining \(x_{LI}\) and \(x_{LH}\) as above any concentration in the composition space may be expressed through values of those two independent measures between zero and infinity.

The following sketch of the bifurcation and thus also of the evolution of limit cycle behaviour will be based on those two parameterized concentrations. First the analysis will be performed with respect to \(x_{LI}\) whereupon the analysis will be proceeded with \(x_{LH}\). The reason for this proceeding, which will become obvious during the qualitative
sketch, is that the behaviour depending upon the latter, $x_{LH}$, is predefined through the former, $x_{LI}$.

### 6.1.1 Influence of $x_{LI}$ on Limit Cycles

During this sketch of the influence of $x_{LI}$ on the bifurcation behaviour, it is assumed that the feed composition lies always outside the $\Omega$-region. This restriction will be abolished in the next section, when, considering $x_{LH}$, the results will be generalized.

If $x_{LI}$ is small, and therefore the distillate product path does not cross the $\Omega$-region, normal, stable behaviour throughout both, the upper and the lower branch of the bifurcation diagram may be observed.

When increasing $x_{LI}$ the distillate product path approaches the $\Omega$-region and at a certain point oscillating behaviour are observed. Finally at the point where the product path touches the boundary of the $\Omega$-region two Hopf bifurcations are born. If now $x_{LI}$ is increased further the distillate product path will cross the $\Omega$-region and the Hopf bifurcations will move apart, allowing for limit cycle behaviour between them. The further the product path enters the $\Omega$-region, the further the Hopf bifurcations move apart, while the amplitude of the limit cycles becomes bigger and bigger.

At a certain point this amplitude becomes that big, that the stability of the limit cycles is lost and the region between the Hopf bifurcations is ripped apart by two homoclinic bifurcations.

With increasing $x_{LI}$ both, homoclinic and Hopf bifurcations move further apart, while the homoclinic tend to push towards the Hopf bifurcations and cause the region which allows for limit cycle behaviour to shrink. Finally the Hopf, the homoclinic and the fold bifurcation corresponding to the lower distillate to feed ratio coincide in one point and the range of limit cycles corresponding to that Hopf bifurcation disappears. The other region of limit cycles will however survive, though it will be relatively small.

### 6.1.2 Influence of $x_{LH}$ on Limit Cycles

$x_{LH}$ has been shown in (Dorn 2000) not to have significant influence on the bifurcations that occur, but only where they occur. This may be explained with the observation that while $x_{LI}$ determines the shape of the product path, $x_{LH}$ only determines where it ends.

When increasing $x_{LH}$ all bifurcations and the corresponding effects are shifted towards a higher distillate to feed ratio until $x_{LH} = x_{LH}^*$. Afterwards, while this shift continues for the fold bifurcation corresponding to lower distillate flow rate the trend will be reversed for the other and the two will be pushed together, wherefore the region of multiple steady states will become smaller. However all other bifurcations are still moving towards higher distillate to feed ratios and eventually they will cross the boundary of physical meaningfulness and occur at distillate to feed ratios greater than one. E.g. this is the case for one of the Hopf bifurcations, when the feed composition enters the $\Omega$-region.

Before this happens for the second Hopf bifurcation as well, there will be a special range in distillate flow rate characterized by the fact that the column does not present a stable steady state but evolves limit cycle behaviour instead. This range can exist if and only if the feed is inside the $\Omega$-region.

The situation that for certain operating conditions no stable steady state but only stable limit cycles exist is very interesting with regard to an experimental set-up. This
feature could be exploited, since it would mean there are not the problems caused by a second, stable steady state.

6.2 Influence of Reflux Flow Rate

The investigation of the influence of changes in the reflux flow rate can not be based on the $\infty/\infty$-analysis as it is possible for the feed composition. Therefore another approach must be found. The main question is to understand how the product profiles and paths change with the transition from infinite to finite reflux. Generally speaking it can be said that decreasing the reflux, the external flow rates start to influence the internal profile and the power of separation decreases. As a consequence the column profiles move away from the residue curves and will be bent less. Therefore the $\Omega$-region becomes smaller.

As suggested in (Dorn 2000), the change in the $\Omega$-region will become the governing effect. With decreasing reflux the $\Omega$-region becomes smaller, which has the same effect as a distillate product path which lies further outside with regard to the $\Omega$-region. The effects introduced by reducing the reflux may therefore qualitatively be related to the effects introduced by reducing the $x_{LF}$.

Although this relation is quite a "crude way" to describe the influence of the reflux, this provides the possibility to characterize the behaviour of the system at least qualitatively. However, it is important to remember that this relation neglects the fact that the $\Omega$-region does not depend linearly on the reflux and its changes are not completely predictable with the simple approach used here.
Chapter 7

Period of Oscillation

In this chapter the influences of design and operating parameters upon the period of oscillation shall be discussed. This discussion includes the qualitative discussion of the previous section only marginally. The results in this chapter are obtained through rigorous numerical simulation with ASPEN RadFrac. After this section control strategies regarding the operation of the column are investigated and their influence upon dynamic behaviour and especially upon limit cycles is discussed in the next chapter.

The simulations are always performed starting from a reference simulation. This reference simulation in the case of the methanol-methylbutyrate-toluene mixture corresponds to the setup presented in Section 4.2, except for two specifications. First the distillate to feed ratio for the reference simulation is set to 0.955, which is not that close to the boundaries of the region where limit cycle behaviour may be observed. On the other hand the thermodynamic properties are estimated by UNIFAC in ASPEN Plus. However the whole set-up is summarized again in Table 7.1.

For the system aceton-benzene-heptane, the reference set-up is the one listed in Table 7.2. The property model used for this system is the Wilson model.

7.1 Model Effects

Before performing a detailed analysis, one of the first points to investigate is the effects that changes of the model introduce, since this analysis has to be carried out with ASPEN RadFrac, while most of the previous work is based on a CMO model. In order to compare the two models, bifurcation diagrams are calculated for both and are then compared in the same diagram.

To draw and to compare a bifurcation diagram a target variable is needed. The distillate concentration of benzene has been chosen. The reason for that choice is that the two branches entering the region of bifurcation are in that case significantly different from each other and maintain this feature almost throughout the whole region of bifurcation. Thus when calculating the two branches up to the points where fold bifurcations occur, the jump to the other branch is most likely to occur only at those points and can be determined easily. This gives the advantages that not only the value of the concentration can be compared but actually also two bifurcation points.

From bifurcation analysis with AUTO, a powerful software package to perform bifurcation analysis, and the CMO model, as base model, the form of the bifurcation diagram has been determined to look as depicted in Figure 7.1. It can be seen, that
CHAPTER 7. PERIOD OF OSCillation

Table 7.1: Reference column set-up for RadFrac simulations with methanol-methylbutyrate-toluene.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>N° of trays (including condenser and reboiler)</td>
<td>46</td>
</tr>
<tr>
<td>Feed tray (counting from condenser)</td>
<td>41</td>
</tr>
<tr>
<td>Column pressure [atm]</td>
<td>1</td>
</tr>
<tr>
<td>Reflux to feed ratio [mole/mole]</td>
<td>12</td>
</tr>
<tr>
<td>Distillate to feed ratio [mole/mole]</td>
<td>0.955</td>
</tr>
<tr>
<td>Feed flow rate [kmol/h]</td>
<td>100.0</td>
</tr>
<tr>
<td>Feed flow rate [kg/h]</td>
<td>4010</td>
</tr>
<tr>
<td>Feed composition methanol (mole fraction)</td>
<td>0.8671</td>
</tr>
<tr>
<td>Feed composition methylbutyrate (mole fraction)</td>
<td>0.0050</td>
</tr>
<tr>
<td>Feed composition toluene (mole fraction)</td>
<td>0.1279</td>
</tr>
<tr>
<td>Column geometry</td>
<td></td>
</tr>
<tr>
<td>Column diameter [m]</td>
<td>2.00</td>
</tr>
<tr>
<td>Weir height [m]</td>
<td>0.07</td>
</tr>
<tr>
<td>Tray spacing [m]</td>
<td>0.61</td>
</tr>
<tr>
<td>Condenser and reboiler</td>
<td></td>
</tr>
<tr>
<td>Vessel type (ends)</td>
<td>flat</td>
</tr>
<tr>
<td>Length [m]</td>
<td>1.0</td>
</tr>
<tr>
<td>Diameter [m]</td>
<td>0.7</td>
</tr>
<tr>
<td>Vapor fraction</td>
<td>50%</td>
</tr>
</tbody>
</table>

There is a clear difference between the upper and the lower branches, while the unstable intermediate branch is quite close to the lower branch.

With ASPEN a continuous path cannot be obtained but only a stepwise determination of the steady states on the upper and the lower branch of the bifurcation diagram can be performed. At each new step the results of the previous run are taken as the initial guesses for the next run in order to ensure that the next solution will remain on the same branch. To start, a point in either single steady state region is calculated and the stable branch is followed with steadily increasing or decreasing the distillate to feed ratio until the jump occurred at the fold bifurcations. Thus the calculations have to be performed twice, once coming from either side.

The results of this analysis are depicted in Figure 7.2, where the results of the ASPEN RadFrac bifurcation diagram are plotted over the original bifurcation diagram obtained with AUTO.

The regions of bifurcations remain the same. No difference was visible in between the bifurcation behaviour of the two models. The conclusion which may be drawn is that the CMO model is a valid model compared to the ASPEN RadFrac model and the results should be reproducible in either model.

However the characteristic Hopf bifurcations can not be retrieved in this way with ASPEN RadFrac. Neither can information about the dynamic behaviour be gathered. Despite this, many important information about the influence of different column design on period of oscillation can be obtained only with ASPEN Dynamics. These influences are the subject analyzed in the following.
Table 7.2: Reference column set-up for RadFrac simulations with acetone-benzene-heptane.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N^{\circ}$ of trays (including condenser and reboiler)</td>
<td>46</td>
</tr>
<tr>
<td>Feed tray (counting from condenser)</td>
<td>41</td>
</tr>
<tr>
<td>Column pressure [atm]</td>
<td>1</td>
</tr>
<tr>
<td>Reflux to feed ratio [mole/mole]</td>
<td>48</td>
</tr>
<tr>
<td>Distillate to feed ratio [mole/mole]</td>
<td>0.925</td>
</tr>
<tr>
<td>Feed flow rate [kmol/h]</td>
<td>0.010</td>
</tr>
<tr>
<td>Feed flow rate [kg/h]</td>
<td>0.624</td>
</tr>
<tr>
<td>Feed composition acetone (mole fraction)</td>
<td>0.8937</td>
</tr>
<tr>
<td>Feed composition benzene (mole fraction)</td>
<td>0.0070</td>
</tr>
<tr>
<td>Feed composition heptane (mole fraction)</td>
<td>0.0993</td>
</tr>
<tr>
<td>Column geometry</td>
<td></td>
</tr>
<tr>
<td>Column diameter [m]</td>
<td>0.0500</td>
</tr>
<tr>
<td>Weir height [m]</td>
<td>0.0125</td>
</tr>
<tr>
<td>Tray spacing [m]</td>
<td>0.1</td>
</tr>
<tr>
<td>Condenser and reboiler</td>
<td></td>
</tr>
<tr>
<td>Vessel type (ends)</td>
<td>flat</td>
</tr>
<tr>
<td>Length [m]</td>
<td>0.04</td>
</tr>
<tr>
<td>Diameter [m]</td>
<td>0.05</td>
</tr>
<tr>
<td>Vapor fraction</td>
<td>50%</td>
</tr>
</tbody>
</table>

7.2 Holdup per Stage

In this section the effects based on the holdup in a tray column will be investigated. First it is explained why holdup should have a big influence on the period of oscillation whereupon results from detailed dynamic simulations are presented.

7.2.1 Characteristic Time of a Distillation Column

Rather than looking at a tray column as a whole, a simple stage is considered here. A schematic drawing of a single stage is provided in Figure 7.3. When looking at one tray, i.e. stage, it can be seen that its holdup $M$ is subject to continuous exchange due to the incoming and leaving material streams $L$ and $G$. This exchange can be characterized by the residence time on the tray, which could be defined as the holdup divided by the sum of the incoming streams. Assuming negligible vapor effects, the ratio $\frac{M}{L}$ represents the residence time of the liquid. Therefore the analysis of the dynamics of limit cycles in distillation columns will be done in terms of the characteristic time defined as:

$$\tau_{\text{char}} = \frac{M}{L} \quad (7.1)$$

This time is the characteristic measure to quantify the exchange on a tray and thus its dynamics. In (Skogestad and Morari 1988) two time constants, different from the one used here, are used to describe the dynamic response of a distillation column. The reason to use a different time constant here is that the oscillations observed are not the results of a response effect but of exchange on the trays. Since the characteristic
time used to describe dynamic effects must be based on the underlying effects, here the characteristic time of a tray is used. In the following the dependence between this time an the period of oscillation will be investigated. The proceeding is sketched in the next section.

### 7.2.2 Determination of Dependence on Characteristic Time of a Tray

To determine the dependence of the period of oscillations on the characteristic time introduced before either the holdup or the reflux have to be varied. However, in Section 6.2 it is shown that limit cycle behaviour and the corresponding bifurcations depend very nonlinearly on the reflux and that upon small changes in the reflux flow rate the limit cycles might disappear. The holdup on the other hand can be varied within quite a wide range without causing limit cycles to disappear.

To vary the holdup in a tray column, there is a design parameter which can be exploited. The holdup on the tray is determined by two quantities, first there is a static holdup due to a weir, which retains liquid on a tray and then there is a dynamic holdup, which arises since the liquid level has to be higher than the weir in order to flow over it. This difference in height between the liquid level and the weir height is called crest and determines the dynamic holdup.

If the weir height is big enough the dynamic holdup may be neglected with regard to the static, since it is much smaller. Furthermore the dynamic holdup does not change significantly if the weir height \( h_w \) is changed as long as the internal flow rates are not changed. The dynamic holdup and thus the crest height \( h_c \) may therefore be assumed to remain constant. This may be explained by the fact that the crest height is determined by the weir length, column internal flow rates and mixture properties only. And since non of the characteristics mentioned before does change upon variations in the weir height (holdup) the assumption of constant crest height must hold. As a consequence the dynamic holdup is also constant.

To conclude, the holdup on a tray may be written as a sum of two terms one of...
which accounts for the static holdup depending on the weir height, whereas the other accounts for the dynamic holdup, which depends on the crest height and therefore indirectly on the reflux and mixture properties. This relationship is sketched in the following equation.

\[ M = A \rho_m (h_w + h_c(L)) \] (7.2)

In this equation \( A \) is the cross section of the column and \( \rho_m \) is the molar density of the mixture. The influence of the mixture properties upon the crest height is not mentioned explicitly in the above equation. Now this relationship may be exploited to investigate the dependence of the period of oscillation upon the characteristic time of a tray. If Equation 7.2 is now inserted into Equation 7.1 for the characteristic time derived before it may be rewritten as:

\[ \tau_{char} = A \rho_m \left( \frac{h_w}{L} + \frac{h_c(L)}{L} \right) \] (7.3)

When looking at this expression it can be seen that the characteristic time of a tray is the sum of two terms, the first one corresponds to the residence time due to the static holdup, while the second term corresponds to the residence time due to the dynamic holdup.

Limit cycle behaviour implies a subsequent change in concentration throughout the whole upper section of the distillation column. The characteristic time which describes the exchange on a single tray is the characteristic time deduced above. The evolution of limit cycle includes the exchange on many coupled trays. It may therefore be claimed that the period of oscillation in a distillation column scales proportionally to the characteristic time of a tray,

\[ \tau_{osc} \sim \alpha \tau_{char} \] (7.4)

the period of oscillation may then be related to the characteristic time of a tray as follows:

\[ \tau_{osc} \sim \alpha A \rho_m \left( \frac{h_w}{L} + \frac{h_c(L)}{L} \right) \] (7.5)
If the reflux is now maintained on a constant level, this expression may be simplified by taking the unknown constants $\alpha$ and $A$ together and substituting the last term through a constant as well.

$$\tau_{osc} \sim C_1 h_w + C_2$$  \hspace{1cm} (7.6)

The coefficients defined in this last equation depend on tray geometry. This is not favorable if several systems with different designs shall be compared. Therefore it would be advantageous to redefine the independent variable such that the constants do not depend on the column geometry anymore. The best variable would be a characteristic time. For further investigation it is therefore looked at the influence of $\frac{\Delta \rho_m}{\rho_m}$ onto the period of oscillation. This ratio represents the residence time of the static holdup.

When looking at $\frac{\Delta \rho_m}{\rho_m}$ it has to be noticed that there is still an uncertainty regarding this measure. While $A$ and $h_w$ remain constant throughout the column, $L$ and $\rho_m$ do not. For $L$ it may be assumed, that the liquid stream entering a tray is equal to the reflux for any tray between condenser and feed tray, which corresponds to the CMO model assumption. Since the feed tray is almost at the very bottom of the column and the reflux to feed ratio is quite big, this is a good approximation for $L$ in general.

Having found a good estimate for $L$, it is focused now on the molar density of the mixture, which changes along the column due to changes in composition. This change mainly occurs in the front, since there is a sharp change in all mixture properties. But the change along the column is not the only effect, it changes also with time, since the column is evolving limit cycle behaviour. The change in time however could be accounted for with a time average and therefore an average molar density for any tray $k$ could be calculated:

$$\rho_m^k = \frac{\int \rho_m^k(t)dt}{\int dt}$$  \hspace{1cm} (7.7)

The question which arises now, is which of these tray average molar densities would be suitable to characterize the oscillations. There are several possibilities, first of all it could be averaged over all trays. This does not make sense as we will see in Section 7.4,
where it is shown that after a certain number of stages any additional stage add to the bottom (pinch point) and does not influence the oscillations anymore. The oscillations mainly occur in the upper section of the column and the trays very close to the bottom do not oscillate significantly. Therefore accounting for those stages in the average density does not make sense. Due to this observations it could be claimed to average the densities of the actually oscillating trays only. But the question in this case is at what amplitude a tray should be considered to be taken into that average. Furthermore this would lead to results which are hard to reproduce and whose underlying assumptions are not intuitively.

Therefore it is chosen to use the molar density which has been obtained in the steady state simulation at the top tray. An additional reason to the ones mentioned before is, that for 001 systems this density is characteristic for the limit cycle behaviour itself. As stated before the oscillations occur mainly towards the top of the column and do have a significant impact on the distillate and top tray composition. Furthermore the distillate composition is a crucial factor for the evolution of limit cycles and when making the time average of the distillate molar density the result should be really close to the steady state distillate density.

Finally this measure is easily reproducible and can be applied to any other system, where oscillations occur mainly in the top of the column, e.g. the whole 001 class.

### 7.2.3 Results

The dependence of the period of oscillations upon the measure derived before has been investigated for two systems. On one hand the mixture of methanol-methylbutyrate-toluene and on the other hand the mixture of acetone-benzene-n-heptane have been studied.

While the results for the first system are summarized in Table 7.3 the ones for the latter are summarized in Table 7.4. The results listed in the tables mentioned before are also visualized in Figure 7.4.

Table 7.3: Dependence of period of oscillation upon residence time in static liquid holdup on a tray for the system methanol-methylbutyrate-toluene.

| \( \frac{\Delta t_{\text{osc}}}{L} \) [h] | 0.000946 | 0.001891 | 0.003782 | 0.007565 |
| \( \tau_{\text{osc}} \) [h] | 35.5 | 42.5 | 56.5 | 84 |

Table 7.4: Dependence of period of oscillation upon residence time in static liquid holdup on a tray for the system acetone-benzene-heptane.

| \( \frac{\Delta t_{\text{osc}}}{L} \) [h] | 0.000678 | 0.001356 | 0.002568 | 0.004108 |
| \( \tau_{\text{osc}} \) [h] | 36 | 52 | 82 | 120 |

It can be seen from the graphs in Figure 7.4 that the assumptions made in the previous section hold. The period of oscillation depends linearly on the characteristic time of a stage according to data obtained by detailed dynamic simulation with ASPEN RadFrac. With a linear regression of the data the results summarized in Table 7.5 were obtained.
Assuming there is no additional term in Equation 7.4 it must be possible to explain the intercept of the graphs shown in Figure 7.4 through the residence time effect in the dynamic holdup only. When calculating the crest height based on the correlation developed in the previous section, it has to be noticed that this crest height is significantly bigger than the “true” one calculated during the simulation. The crest height calculated was found to be physically meaningless. It must be concluded that there is an additional term in Equation 7.4, which can be reformulated as follows:

\[
\tau_{osc} = \alpha \tau_{char} + \tau_0
\]  

(7.8)

The term \(\tau_0\) may be interpreted as intrinsic time of oscillation which corresponds to the minimal period of oscillation for a specific mixture and set-up. As a consequence there seems to be a limit for the reduction of the period of oscillation. Nevertheless, it is necessary to reduce the holdup as far as possible in order to approach the minimal time of oscillations. This may achieved in different ways. One of the most efficient ways to reduce holdup would be to switch to packed columns. Therefore the dependency developed in Equation 7.8 will be extended to the case of packed columns and predictions about the influences of the results obtained here will be made.
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7.3 The Holdup in a Packed Column

As it has been shown in Section 7.2.2 the period of oscillations is heavily dependent on the holdup in the distillation column. According to the predictions and to the simulations performed it would be favorable to reduce the holdup in the column as far as possible. This may be achieved by switching the set-up from a tray column to a packed column. However the concept developed in the previous section must be worked out for a packed column in order to see how the time of oscillation can be influenced.

The relation between the reflux and the holdup are investigated using first theoretical predictions, therefore correlations available in literature and second a design tool provided by Sulzer Chemtech. Sulzer Chemtech is a technical company producing the packings for distillation columns including the packings intended to be used for the experimental column.

7.3.1 Theoretical Predictions

In literature there exist many correlations to predict the holdup of a packed column. Most of them are held in terms of dimensionless numbers. Probably one of the most widely used, is the one developed in (Engel, Stichelmair and Geipel 1997):

\[
m = 0.93 \left( \frac{u_L \alpha}{g} \right)^\frac{1}{6} \left( \frac{\eta_L \alpha^3}{\rho_L g} \right)^\frac{1}{3} \left( \frac{\sigma \alpha^2}{\rho_L g} \right)^\frac{1}{3}
\]

where \( m \) is the volume fraction for the packing which is occupied by the liquid. \( u_L \) is the superficial velocity of the liquid, \( \rho_L \) is the density, \( \eta_L \) the viscosity and \( \sigma \) is the surface tension of the liquid. \( \alpha \) is the surface area per unit volume and \( g \) is the acceleration due to gravity. As it can seen in this expression the volume fraction of liquid in a packed column, and therefore the holdup, depends on many different properties of the mixture. Since it is the goal of this work to prepare the experimental validation of limit cycles it is mainly looked at the dependence of the holdup upon operating parameters. The only operating parameter except for packing properties which can thought to influence the volume fraction occupied by the liquid and thus the holdup is the reflux flow rate. Therefore a relationship between holdup and reflux will be deduced here.

The only variable depending on the reflux is the velocity. Therefore it is possible to group all the other terms in a coefficient \( \gamma \) obtaining:

\[
m = \gamma u_L^\frac{1}{6}
\]

To construct a relation to the reflux flow rate the superficial velocity \( u_L \) must now be expressed as a function of the reflux.

\[
L = m u_L \rho_m A
\]

Therefore the following expression may be obtained:

\[
m = \gamma \left( \frac{L}{\rho_m A} \right)^\frac{1}{6}
\]

In order to insert this expression into the definition of the characteristic time of a tray, the correspondence of a tray to a theoretical stage in a packed column has to be used.
Therefore to obtain the holdup, the volume fraction occupied by liquid, has to be multiplied with the height of a theoretical stage and the cross section of the column. Inserting everything into Equation 7.1 we obtain:

\[ \tau_{\text{char}} = \gamma \frac{h_{\text{theo}}}{L} \left( \rho_{m} \frac{A}{L} \right) \]

Inserting this result into the revised relationship for the period of oscillation finally the following dependence is obtained:

\[ \tau_{\text{osc}} = \alpha \gamma \frac{h_{\text{theo}}}{L} + \tau_{0} \]

Revisiting Equation 7.10 it may be noticed that \( \gamma \) only contains thermodynamic properties and packing characteristics. Therefore the influence of the reflux upon this measure may be assumed to be negligible. Neither should \( \rho_{m} \) depend on reflux. So \( \alpha \), \( \gamma \), and \( \rho_{m} \) may be taken together into a constant \( \delta \) to lead to the following expression:

\[ \tau_{\text{osc}} = \frac{\delta h_{\text{theo}}}{L} + \tau_{0} \]

The only variable which cannot be assumed to change negligibly with reflux is the height of a theoretical stage. This height increases with increasing reflux. However the relationship between \( h_{\text{theo}} \) and the reflux is by no means linear and depends heavily on the packing. Nevertheless, the rise in the theoretical stage height introduced by a change of the reflux \( L \) should not be as big as the change of \( L^{\frac{\delta}{\gamma}} \). Therefore through the increase of reflux, the period of oscillation should decrease. Only towards the flooding point of the column the operating efficiency drops dramatically and the height of a theoretical stage increases rapidly. The effect of increasing \( h_{\text{theo}} \) will then be that high, that instead of reducing the period of oscillation with increasing reflux, it will be prolonged.

These conclusions drawn here are not free of concerns. As it has been shown in Section 6.2 variations in the reflux flow rate have a big implication on the region wherein limit cycle behaviour occur. Only a slight change in the reflux flow rate might cause the system not to evolve limit cycles anymore. Therefore the applicability of the correlation developed in Equation 7.15 is restricted by the limitations implied by the changes in bifurcation behaviour with the reflux.

### 7.3.2 Validation of the theoretical Results through Sulpak

The results obtained in the previous sections are based on correlations. Since these are very general, it is not exactly known whether these correlations are able to predict the behaviour of the experimental packing correctly, this must be validated.

For the experimental set-up a packing of Sulzer Chemtech is most probably to be used, wherefore Sulpak is used to verify the behaviour of the holdup in dependence of the reflux. Sulpak is a software package provided by Sulzer Chemtech which allows to determine holdups in their packings.

The whole derivation of Equation 7.15 is based on the assumption, that the volume fraction of the packing occupied by the liquid \( m \) would behave as in Equation 7.10 and could be reformulated to the expression obtained in Equation 7.12. With Sulpak it has
been tried to validate this dependency of the holdup upon the reflux. The following proportionality has been found:

\[ m \sim L^\beta \]

Using this result it must be concluded that the dependency of the period of oscillation should scale as follows with the reflux:

\[ \tau_{osc} = \delta \frac{h_{thef}}{L^\beta} + \tau_0 \]  

(7.16)

Despite this result is not the same as the one obtained with Equation 7.15, the only difference is the exponent of the reflux. This difference is explained by the fact that with Sulpak a specific packing is considered while in the previous section general equations are applied. Nevertheless the qualitative effects described in the previous section should still hold. Only the extent to which they occur will change.

### 7.4 Number of Stages

The number of stages in a distillation column has a big influence on the operation of the column, since it determines what separations will be feasible and is therefore a crucial design parameter. On the other hand the number of stages determines the size of a column which is actually restricted by laboratory facilities wherefore the number of stages which can be used for the experimental set-up is not unlimited.

Generally speaking a bigger number of stages allows for a better separation, and therefore other compositions could be achieved during oscillations, which might influence their behaviour significantly. On the other hand, if too low a number of stages is used, it might be impossible to build up the column profiles necessary to evolve limit cycle behaviour. Since it is already known from previous work that there is a minimum number of stages necessary, here it is focused on the effects which would occur if the number of stages is increased.

#### 7.4.1 Steady State Effects

First of all steady state calculations for different number of stages have to be performed and the results to be compared. The column profiles do not differ upon a first look, as can be seen in Figure 7.5. Upon a closer look near to the pinch point in the column profile it can be seen that there are differencies regarding how much the column profiles would approach the pinch point, as it is expected. It can be seen in Figure 7.6 that the bottom composition actually gets closer to pure heavy component. The importance of this observation will be seen in Section 7.5, where effects regarding reboiler and condenser size will be discussed.

However, the steady state simulations have been found to behave as expected. To investigate the dynamic influences of the number of stages dynamic simulations have to be run for column set-ups with different number of stages. While the original columns are laid out quite at the limit that allows for limit cycle behaviour, the other columns simulated are designed to have significantly more stages. The results will be discussed in the next section.
7.4.2 Dynamic Effects

Simulating columns with 46, 69 and 138 stages respectively, it has been found that increasing of the number of stages, the period of oscillations first increases quite strongly, whereupon it remains constant. The periods of oscillations observed are summarized in Table 7.6.

Table 7.6: Period of oscillation with regard to the number of stages for the system methanol - methylbutyrate - toluene.

<table>
<thead>
<tr>
<th>Number of Stages</th>
<th>46</th>
<th>69</th>
<th>138</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period of Oscillation</td>
<td>55</td>
<td>110</td>
<td>110</td>
</tr>
</tbody>
</table>

When looking only at the period of oscillation it would be favorable to work at the lowest possible number of stages which still allows for limit cycle behaviour. This conclusion is not completely correct since there are other effects influencing the applicability in reality.

When looking at the evolution of limit cycles which is depicted in Figure 7.7 for the composition space and in Figure 7.8 for the time dependence, it can be noticed that the limit cycles evolve much quicker in the case of 69 stages than in the case of 46 stages, when starting from the steady state solution as initial condition.

While for 46 stages about twenty oscillations are needed to obtain the full limit cycle amplitude, for the case with 69 stages only about three are needed which is equivalent to a much shorter startup time. However when going to 138 stages this number, i.e. the startup time, could not be decreased further but the period of oscillations still increased. Thus it must be assumed that the change in the amount of oscillations needed...
to reach the full limit cycle behaviour occurs soon after having some more than the minimal number of stages necessary.

Based on the results presented before an optimal number of stages must be found where the trade off between reducing the startup time and increasing the period of oscillations, in order to obtain an optimal total experiment duration, which allows for sensible realization. On the other hand there is an additional restriction which must not be forgotten due to laboratory facilities upon the height of the column and thus upon the number of stages which cannot be violated.

This is a task which has to be carried out in the final design of the experimental set-up.

### 7.5 Size of Reboiler and Condenser

After having looked at the stages in general it is looked now at two special stages. So far reboiler and condenser have not been modeled realistically, they were just modeled as additional stages which is not quite true since this neglects the fact that reboiler and condenser are designed substantially different from a stage in reality.

#### 7.5.1 Real Condensers

In practice condensers consist of the condensing section itself and a reflux drum. Whereas the vapor is condensed in the condensing section and collected thereafter in the reflux drum. The reflux drum is usually used to dampen flow variations and to reduce variations in the distillate composition.
Since the condensing section of the condenser is mainly filled with vapor the corresponding holdup may be assumed to be small with regard to the holdup of the reflux drum which is filled with liquid. Furthermore the holdup of a reflux drum is usually comparably big since it is generally used to damp variations. In (Faanes and Skogestad 2000) it is referred to different residence times in reflux drums in order to perform this task successfully. Those referred residence times range in between 2 and 30 minutes.

Since we would like to measure oscillations a damping effect upon our system is not desirable. Obviously it is therefore necessary to reduce the damping effect of our condenser and therefore of our reflux drum as far as possible and thus to reduce its holdup in order to maintain limit cycle behaviour. Although with this conclusion already a qualitative design guideline could be deduced it is nevertheless major interest to calculate, when the damping effect becomes important, in order to know where system limitations lie.

A further problem in this area is that a reflux drum is desirable to operate the experimental column since it is much easiest to withdraw our distillate product stream as a saturated liquid stream, especially if a certain accuracy is required. The withdrawal of a vapor stream is much more complicated due to the fact that exact measurement for vapor streams are hard to accomplish and this accuracy would have to be accounted for by dramatically increasing effort. Therefore is preferable to withdraw the distillate product as a liquid stream. To do this, the liquid must be collected somewhere in the distillation column, wherefore a reflux drum is needed. However the reduction of its holdup can be performed rigorously and should not cause a problem.
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Figure 7.8: Evolution of limit cycle behaviour for 46 and 69 stages respectively in dependence of time.

7.5.2 Real Reboilers

Reboilers can be designed quite compact and their holdup is mainly determined by their design. Usually there is no additional vessel like a reflux drum for the condenser, since the leaving stream can be controlled quite directly and accurately by the reboiler duty. Further more the damping effect can be achieved by the design of the reboiler itself, which would then be laid out with quite a big volume. Nevertheless the holdup of a reboiler is usually quite large, since it consists mainly of liquid. As for the condenser, also in the case of the reboiler it is not desirable to have any damping effect and as a consequence any reduction of the reboiler holdup would be favorable.

7.5.3 Investigated Variables

The focus of the investigations in this area was directed to the following to ratios:

\[
\frac{M_{\text{cond}}}{M_{\text{stage}}} 
\]

(7.17)

and

\[
\frac{M_{\text{reboiler}}}{M_{\text{stage}}} 
\]

(7.18)

Where \(M_{\text{cond}}\) and \(M_{\text{reboiler}}\) are the holdups of the condenser and the reboiler respectively and \(M_{\text{stage}}\) is the holdup of one stage.

As it has been shown in Section 7.2, the time which best relates the period of oscillation to dynamics within the column is the characteristic time of exchange on one tray, thus \(\frac{M}{L}\). It has to be kept in mind, that \(M\) in this relationship is the holdup of a stage. For clearness this quantity was changed to \(M_{\text{stage}}\) in the expressions above. To describe the dynamics of the condenser and the reboiler, it would be favorable to refer to a variable similar to a characteristic time, their residence time. As distillate and feed are comparably small to the column internal flows in the cases investigated here, these residence times may be approximated as the ratios of the holdups and the reflux. If this
approximated residence time is now compared with the measure of the characteristic time of a tray, the reflux flow rate can be canceled and the comparison reduces to the comparison of the corresponding holdups.

For the reasons cited in the previous paragraph the two ratios defined above correspond to a comparison of the dynamics in the reboiler and in the condenser respectively with the dynamics on a tray. At the meantime they also refer to core design properties of reboiler and condenser and thus give us good measures for a later design of this equipment.

Again it is emphasized that this approach may be problematic, since it assumes that the residence times are determined by the reflux flow rate, which is not totally correct. All the simulations assumed a feed stream at its bubble point, thus the flow rate to determine the residence time of the reboiler should be bigger by about the feed stream, wherefore the residence time would decrease. For the condenser the residence time should be smaller, too, since it is neglected that the distillate stream is withdrawn. This effect may be neglected though because this work is dealing with very high reflux ratios and the errors introduced by not accounting for the feed flow rate or the distillate are relatively small. Furthermore the point of interest is the qualitative behaviour and thus a small error may be accepted as long as it does not influence the qualitative results.

7.5.4 Results

The analysis of the influence of $\frac{M_{\text{cond}}}{M_{\text{stage}}}$ and $\frac{M_{\text{reb}}}{M_{\text{stage}}}$ was performed with the CMO model on one hand for acetone-benzene-heptane and methanol-methylbutyrate-toluene on the other hand with ASPEN Dynamics.

The results obtained for both set-up showed the same qualitative behaviour, which will be discussed now. When increasing the holdups it was noticed that the limit cycle behaviour disappeared at some critical values for the holdups. These will be called $H_{c, \text{cond}}$ for the condenser and $H_{c, \text{reb}}$ for the reboiler respectively. Therefore if those critical values where exceeded for a specific system the steady state of that system whose former character was that of an unstable focus changed to that of a stable focus and no limit cycle behaviour could be observed anymore. Thus the real parts of the eigenvalues crossed the imaginary axis and the steady state solutions changed from an unstable steady state with limit cycle behaviour to oscillating behaviour around a stable steady state (focus).

The critical values for condenser and reboiler holdup respectively are listed in Table 7.7. What is most interesting about these is the asymmetry in the results and the dependence of the critical reboiler holdup upon the number of stages. Another very interesting fact about those critical holdups was that the critical holdup for the reboiler which is just denoted as a function of the number of stages in the table cited before is actually always significantly bigger as the critical holdup for the condenser. In the next section these results will be explained better.

Table 7.7: Critical Holdups $H_{c, \text{cond}}$ and $H_{c, \text{reb}}$ for which the limit cycle behaviour vanishes.

<table>
<thead>
<tr>
<th></th>
<th>$H_{c, \text{cond}}$</th>
<th>$H_{c, \text{reb}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMO model, ABH</td>
<td>50 - 100</td>
<td>$f (N_S)$</td>
</tr>
<tr>
<td>ASPEN, MMBT</td>
<td>10 - 20</td>
<td>$f (N_S)$</td>
</tr>
</tbody>
</table>
7.5.5 Explanation

When looking at the oscillation in the column it can be noticed that they mainly evolve closely to the front in the distillation column. In Figure 7.5, where the column profiles are depicted for two cases it can be seen, that the front in the distillation column will be close to the top of the column. This fact can also be derived from theory (Dorn 2000). Towards the lower end of the column, thus towards the bottom product, the column profile does not change very much. From the $\infty/\infty$-analysis it could be derived that the actual pinch point in a distillation column set-up to achieve a configuration which allows for limit cycle behaviour in the case of a mixture of the class 001 is actually at pure heavy component, thus at the bottom of the column. The behaviour of a column profile when approaching pinch points can be summarized with the conclusion that composition does hardly change anymore.

To understand the effects observed, it is necessary to understand the behaviour, when adding new stages to a column whose profile is set up as shown in Figure 7.5. There are two main restrictions upon the ending points of the profile. First there is the material balance which must be fulfilled and secondly the separation must be feasible with the column set-up available. When adding additional stages to an existing set-up, the bottom and the distillate composition move further apart and will lie on a residue curve which is bent more. However this can only continue until the profile contains a pinch point. If this is the case, distillate and bottom cannot move further apart and any additional stage will be consumed in the pinch. In reality pinch points cannot not be reached, since an infinite number of stages would be needed. Therefore once the column profile approaches a profile containing a pinch point the additional stages are consumed approaching the pinch, which does not lead to a significant change of composition though.

The consequences of this behaviour when adding new stages is that the bottom composition in the steady state case approaches pure heavy component with increasing number of stages. However this effect must also hold somehow for the dynamic case. It can be concluded that with increasing number of stages the composition at the bottom during dynamic simulation must become more and more constant and finally in the limiting case of an infinite number of stages it must remain constant. The qualitative dynamic analysis presented in (Dorn 2000) was actually based on a case of infinite number of stages. However, when looking at the phenomenon it must be concluded that if the number of stages is increased enough the limit cycle behaviour cannot be influenced anymore by any damping effect in the reboiler, since the concentrations and temperature are constant there anyway.

This is not true for the condenser. As it has been shown, an increase in the number of stages does not influence the amount of trays between the front and the very top of the column, since all the additional trays are consumed in the pinch, and thus at the bottom. For Illustration it is referred to Figures 7.6 and 7.9, where the top and the bottom part of the column profile are sketched.

The oscillations of compositions therefore mainly occur in the upper part of the column, i.e. quite close to the very top. Thus a damping effect does have a big impact if applied to the top of our distillation column, i.e. in the condenser, as it has been found in simulations.
CHAPTER 7. PERIOD OF OSCILLATION

7.5.6 Conclusion

The conclusion which may be drawn from those findings is that for an experimental set-up it would first of all be convenient to work at a higher number of stages than the minimal necessary to accomplish the requirements for limit cycle behaviour. With those additional stages a certain security could be gained that the reboiler holdup will not influence the oscillations.

On the other hand it can be clearly stated that the two pieces of equipment, both, the reboiler and the condenser have to be designed to have a holdup which is as small as possible. Although it has been shown that this is not important for the reboiler, if there are enough stages, it should nevertheless not be neglected due to the fact that there are still many uncertainties in the system and it should be tried to avoid introducing damping effects even if they are known not to be likely.

The condenser holdup was found to be a very sensitive parameter with regard to limit cycle behaviour and may cause their disappearance. Thus it is crucial for an experimental set-up to design the reflux drum of the condenser as small as possible, which means that it should be just big enough to withdraw the distillate stream. Ideally the holdup of the reflux drum would be reduced down to the order of magnitude of the holdup of one stage or even lower.

In order to understand what would happen if those design guidelines presented in this conclusion would be neglected or an error would occur in the experimental setup, it is investigated in the next section how the bifurcation behaviour changes in the case when the reflux drum is actually designed too big.

7.6 Behaviour with Excessive Condenser Holdup

In this section the behaviour of a system shall be analyzed which is subject to the phenomena described in Section 7.5. The system discussed here has been laid out to have a condenser characterize by too big a holdup to allow for limit cycle behaviour.
In contrast to the investigations in Section 7.5 these investigations discussed here will be carried out with the mixture acetone-benzene-heptane. The results can however be extended easily to other mixtures. The motivation for this investigation is not straight forward. There is not much interest in investigating a system which does not evolve limit cycle behaviour, when limit cycle behaviour shall be measured. The basic idea is to check if it is possible to get limit cycle behaviour by varying the operating parameters for a system, which has been laid out violating the design guidelines given in the last section and therefore would not show limit cycle behaviour at the original layout conditions. This could for instance happen if the thermodynamic data was not exact enough and thus the system would be designed for the "wrong" mixture. If it is possible to get oscillations anyhow, this would be a big advantage, since the whole experimental set-up would not be worthless.

### 7.6.1 Column Set-Up

The column set-up used to investigate this behaviour had obviously to be changed. The actual dimensions may be retrieved from Table 7.8. As it can be seen the ratio between the condenser holdup and the tray holdup is about 50 times bigger than in the reference case. This set-up was expected to result in damped oscillations.

<table>
<thead>
<tr>
<th>weir height [m]</th>
<th>0.005</th>
</tr>
</thead>
<tbody>
<tr>
<td>reboiler and condenser geometry</td>
<td></td>
</tr>
<tr>
<td>length [m]</td>
<td>0.2</td>
</tr>
<tr>
<td>height [m]</td>
<td>0.15</td>
</tr>
<tr>
<td>vapor fraction</td>
<td>50%</td>
</tr>
</tbody>
</table>

### 7.6.2 Results

The behaviour of the system described in the previous section was analyzed with respect to its dependence upon distillate to feed ratio $D$ and reflux to feed ratio $R$. The investigated points are summarized in Table 7.9. It must be emphasized that no limit cycle behaviour could be observed. The behaviour was either the one of a stable focus or an unstable focus. In the case of an unstable focus the system dropped to the other, stable steady state on the lower branch of the bifurcation diagram.

The characteristic behaviour documented in the Table 7.9 is illustrated as well in Figure 7.10.

### 7.6.3 Conclusions

Although no limit cycle behaviour has been found it is not sure whether there might arise limit cycle behaviour in the region of transition from a stable focus to an unstable focus, since it is not sure whether there is a Hopf bifurcation between the two regions of stability or not. Furthermore the resolution with regard to the reflux is quite low, wherefore limit cycle behaviour could have been missed. If there is a Hopf bifurcation
Figure 7.10: Characteristic behaviour of the system when the condenser holdup exceeds the critical holdup. Circles indicate unstable foci whereas filled circles indicate stable foci.

Table 7.9: Characteristic behaviour of the system when the condenser holdup exceeds the critical holdup. US indicates an unstable focus, whereas S indicates a stable focus.

<table>
<thead>
<tr>
<th>D</th>
<th>0.915</th>
<th>0.9175</th>
<th>0.92</th>
<th>0.925</th>
<th>0.93</th>
<th>0.9325</th>
<th>0.935</th>
<th>0.94</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=48</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R=60</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R=70</td>
<td>S</td>
<td>US</td>
<td>US</td>
<td>S</td>
<td>S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R=100</td>
<td>US</td>
<td>US</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

with an according region of limit cycle behaviour, it is very narrow and can probably not be accessed in an experimental setup. Therefore for an experimental set-up it must definitely be taken care that the critical values for reboiler and condenser are not exceeded. Since if they are exceeded the damping effect in the condenser cannot be compensated through an increase in the reflux. Such an increase would just drive the system into instability but not into limit cycle behaviour.

### 7.7 Distillate Flow Rate

The distillate flow rate is usually used to operate a distillation column. During bifurcation analysis it is used as a bifurcation parameter. It has been found during those analysis, that the range of distillate flow rates wherein limit cycle behaviour occurs is actually quite narrow for a given column design. Nevertheless it may still be varied within this range in order to influence the period of oscillation.

To obtain results which could be used in a more general framework and not only in a specific column set-up, the distillate to feed ratio has been used for the investigations.
7.7.1 Results

The distillate to feed ratio has been varied for the system methanol - methylbutyrate-toluene around the reference case, throughout the whole region of limit cycle behaviour. It has been found that the period of oscillation showed nonlinear dependence on the distillate flow rate. The results are summarized in Table 7.10.

Table 7.10: Period of oscillations for the mixture methanol-methylbutyrate-toluene in dependence of the distillate flow rate.

<table>
<thead>
<tr>
<th>( \frac{D}{F} )</th>
<th>0.959</th>
<th>0.958</th>
<th>0.955</th>
<th>0.9525</th>
<th>0.95</th>
<th>0.945</th>
<th>0.94</th>
<th>93.875</th>
<th>0.93811</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period no</td>
<td>50</td>
<td>65</td>
<td>68</td>
<td>71</td>
<td>76</td>
<td>82</td>
<td>80</td>
<td>no</td>
<td></td>
</tr>
</tbody>
</table>

The data obtained are visualized in Figure 7.11. It can be seen, that the influence of the distillate flow rate on the period of oscillation is not as strong as the dependency on the holdup seen in Section 7.2. Only towards the limits of the region showing limit cycle behaviour it becomes stronger. With respect to the experimental set-up this strong dependence found towards the boundaries mentioned before cannot be exploited to reduce the period of oscillation. While it is obvious that it would be better to work very close to the boundaries of the region in order to achieve a minimal period of oscillations, it must be bared in mind that during an experimental set-up this accuracy of the distillate to feed flow ratio is restricted. But this is not the only problem. The main problem will be that an experimental system is always subject to disturbances and working close to the boundaries mentioned above means to have a high sensitive towards those disturbances. Therefore it is advantageous not to work too close to the boundary because this would imply that one might lose the limit cycle behaviour.

However there is a general tendency which can be seen in the diagram. While the period of oscillations decreases with increasing distillate to feed ratio over a wide range, the range wherein the period of oscillation decreases with decreasing distillate to feed ratio is much smaller. Therefore it might be favorable, to try to increase the distillate to feed ratio once an experimental setup is found which seems to evolve limit cycle behaviour before the actual experiment for validation is carried out.

7.7.2 Numerical Problems

During simulation a peculiar problem has been encountered. Due to the form of the graph depicted in Figure 7.11 it is assumed that there might be a subcritical Hopf bifurcation at the lower end of the region of limit cycle behaviour depicted in that figure. In order to investigate that assumption it has been tried to determine the lower boundary as accurately as possible and thus a set of simulations has been launched in order to determine the point where the two governing eigenvalues of the system would change sign an thus the stability character of the steady state solution would change.

When approaching this point we noticed at a distillate to feed ratio of 0.938115 that the stability character of the steady state solution changed with changing maximum step length of the integrator used for the dynamic simulations. The integrator used is the
7.8 Feed Stage

The feed stage should not have an influence onto the dynamics of oscillations since the feed positions does not change anything significantly in the column, because the internal flow rate are comparably big to the external ones. The only effect which could happen is that if the location of the feed stage is changed too much it could lead to a breakdown of the concentration profile in the column which is necessary to have limit
cycle behaviour and one could drop down onto the other concentration profile which only allows for a stable steady state.

7.8.1 Results

The feed stage position in the column has no influence on the oscillations. Also the influence onto the column profile is quite small, due to the fact that in order to have limit cycle behaviour the column is operated at quite high reflux flow rates. However, the feed should not be moved into to the front inside the column in order to prevent a break down in the column, thus it should be placed in the lower section of the column preferably somewhere around 15% of total height from below.
Chapter 8

Amplitude and Period of Oscillation

When looking at oscillations in general, very often the time scale and therefore the period of the oscillations is intimately connected to their amplitude. The oscillations in a distillation column are based on a transport effect of material into the distillation column and out again, while the bigger the amplitude is, the bigger this effect has to be and probably the bigger is the time necessary. Therefore this relationship between period and amplitude should also hold in the case of a distillation column.

In Figure 8.1 versus the period of oscillation is plotted the amplitude for several distillation columns. The amplitude of oscillation is defined as the maximal difference in light component mole fraction in the distillate during one cycle. The points are for two different systems, acetone-benzene-n-heptane on one hand, and methanol-methylbutyrate-toluene on the other hand. Unfortunately only a few points are available in this graph, but nevertheless, there seems to be a tight correlation between amplitude and period of oscillation. Although for the former system only two points are depicted, they seem to follow a similar behaviour: decreasing period of oscillation with decreasing amplitude.

However this must be put into perspective since there might also be other effects influencing the period of oscillation. When now the holdup is changed the amplitude remains constant, since the power of separation in the column (at least for an equilibrium model) remains unchanged. However, since the mass which has to be transported into the region of oscillation and out again is significantly smaller, the holdup is smaller and the period decreases without a change in the amplitude. This behaviour has been validated through simulations and is illustrated in Figure 8.2.

With respect to that finding the points plotted in Figure 8.1 must be revisited. The columns for acetone-benzene-n-heptane and methanol-methylbutyrate-toluene are actually laid out quite differently, i.e. the values of the characteristic times as defined in Section 7.2 are different. This would imply a significantly different period of oscillation, which is not the case. Therefore there must also be a system specific driving force, which influences the period of oscillation.
8.1 Conclusion

To summarize, there are two effects which influence the period of oscillation, mass transfer and driving force. The mass transfer necessarily depends on the amplitude on one hand and it is influenced by the holdup on the other hand. The driving force to move the system around a limit cycle is specific for every mixture.

To minimize the period of oscillation two approaches could now be applied. First it could be looked on the period of oscillation directly, which is done in the investigations presented in Chapter 7. The other approach would be to minimize the amplitude of oscillation, in order to reduce the period.

To minimize the period of oscillation through the amplitude is however not free of concerns, since it is indirect and could therefore be misleading. Furthermore there are additional complications regarding the definition of an amplitude. It has to be decided where in the column it shall be measured and upon which oscillations it shall be measured. E.g. in the previous section the amplitude was defined as the maximal difference in the mole fraction of the light component in the distillate during one cycle of oscillation. Such a definition involves however the column set-up and might therefore be affected by a change of the column set-up this could lead to a wrong conclusion.

Furthermore an approach based on the amplitude of oscillation could not detect changes due to changes in the driving force for oscillation and can therefore not be used to compare two different systems regarding their applicability for an experimental validation of limit cycles in homogeneous azeotropic distillation.
Figure 8.2: Effect of holdup on period-amplitude relationship
Chapter 9

Influence of Specifications on Limit Cycles

For the experimental set-up it was most crucial to know how the system would behave if the original specifications made in the CMO model would be substituted by specifications which would represent an experimental set-up much closer. When looking at the CMO model in its original form, one notices that one of the degrees of freedom specified to calculate was the reflux flow rate. If this specification is compared to the way most real distillation columns are operated it has to be noticed that instead of controlling the reflux flow rate, most often the reboiler duty is controlled instead.

On the other hand all flow rates have been specified in molar terms so far. In practice this approach normally does not hold. Flow rates are either measured in volumetric or in gravimetric terms. Therefore it has to be clarified what influence a specification in those terms would have. This is especially of big concern since in (Jacobsen and Skogestad 1991) output multiplicities are reported which are due to the nonlinear mass mole relationship.

Because of these two reasons it has been decided to substitute some of the fixed degrees of freedom with different expressions in order to see whether limit cycle behaviour would be influenced and if, how.

9.1 Modeling the Reboiler

As it is shown in the theoretical background provided with this work, there are usually two degrees of freedom in a distillation column model. In the bifurcation analysis performed here, the distillate flow rate is used as bifurcation parameter, wherefore only one degree of freedom is left to be specified. The usual choice to specify this parameter in the case of the CMO model is by fixing reflux stream $L$ or a reflux ratio $R$.

Instead of fixing the reflux stream in the column, other expressions could be introduced in order to specify the remaining degree of freedom. One possibility is based on the specification of the reboiler duty, which determines the boilup. Since the bifurcation analysis are performed with the CMO model, which assumes constant molar flows along the column, and since the feed is assumed to be saturated liquid, the reflux is simply given by the difference of the boilup and the distillate flow rate.

Two different strategies to fix the reboiler duty are described in the following. For both of them the influences on bifurcation and oscillations are studied. The two
models and the results obtained are presented in the next subsections.

9.1.1 Constant Heat Load

A very simple but at the same time very powerful model to describe a reboiler is the assumption of a constant heat flux fed to the reboiler. This kind of reboiler may be realised with heating candles where the duty can be controlled through electrical energy fed to the heating candles.

\[ Q_{reb} = \text{const.} \]

The average heat of vaporization of a mixture with composition \( x \) and \( n_c \) components (under the assumption of an ideal mixture) can be estimated as follows:

\[ \Delta \tilde{H}^{\text{vap}} = \sum_{i=1}^{n_c} \Delta H_i^{\text{vap}} x_i \]

Where \( \Delta H_i^{\text{vap}} \) are the related heats of vaporization of the pure components. The boilup (vapor flow rate just above the reboiler) is therefore given by:

\[ V' = \frac{Q_m}{\Delta \tilde{H}^{\text{vap}}} \]

Taking the feed streams into account and subtracting the distillate flow rate it is obtained under CMO assumption:

\[ L = V' + \sum_{k=1}^{n} q^{k} F^k - D \]

Now a complete set of equations is available to substitute the specification of the reflux through a specification of the reboiler duty. In the next section a similar model will be derived but that will not assume constant reboiler duty anymore. Afterwards the results will be discussed.

9.1.2 Constant Utility Temperature

Instead of assuming a constant heat flux, the reboiler could also be modeled as a heat exchanger, using a driving force expression with transfer coefficient.

\[ Q_{reb} = U A \Delta T \]

Assuming a constant heat transfer coefficient, heat transfer area and a constant utility temperature the above equation simplifies to the following expression:

\[ Q_{reb} = k (T_{utility} - T_{reboiler}) \]

Having derived these equations to describe the reboiler duty it is just a matter of repeating the steps performed in the previous section in order to obtain a set of equations which again is suitable to substitute the specification of the reflux. The only difference in this case is that instead of specifying the reboiler duty directly this time the temperature of the utility used to heat the reboiler was specified and a linear heat transfer relationship was assumed.
A big advantage of this last model is that effects between an oscillating interior of the column and its constant outside can be investigated. However this will have a minor effect, since the temperature in the reboiler was found to vary only negligibly due to the character of the column profile.

In the next section the effects of the two different reboiler models upon the bifurcation behaviour will be discussed wherefore the behaviour of the original model with specified reflux flow rate will be described.

9.2 Comparison with the Original Model

The probably most interesting question about these new models is how they influence the region of multiple steady states and the points where bifurcations occur. These questions will be investigated separately for each model in this section.

During this investigations, which are performed with the software package AUTO, the distillate flow rate is the bifurcation parameter, which therefore is varied over the range where bifurcations are expected to occur. This is done at a specified feed and different reflux specifications depending on the reboiler set-up. The results obtained are compared with each other thereafter.

9.2.1 Results of the Original Model

In order to be able to make comparisons with the original model, its behaviour must be known. Therefore bifurcation diagrams have been calculated for the original set-up with specified reflux flow rate. The results may be seen in Figure 9.1. The bifurcation diagrams depicted are one for every component, thus for acetone, benzene and n-heptane and one for the average temperature in the column, which is defined as follows.

\[ T_{\text{avg}} = \frac{\sum_{i=1}^{N_e} T_i}{N_g} \]  

(9.1)

9.2.2 Results at Constant Heat

As it has been shown in Section 6.2 the reflux has a big impact upon the bifurcation behaviour and may introduce a shift of the region or even the disappearance of limit cycles. Due to that influence of the reflux flow rate, the reboiler heat duty has been chosen such that the resulting reflux is approximately the same in the region of concern.

It can be noticed that the reflux remains approximately constant throughout the region of concern, thus along the upper branch of the temperature bifurcation diagram. This may be explained with the bottom composition, which varies only negligibly in that region wherefore the boilup remains constant as well. Therefore the change in the bifurcation behaviour is not expected to be significant. This is confirmed by simulations. Figure 9.3 shows that the two bifurcations diagrams hardly differ. Also, it was validated that the Hopf bifurcation points occur at the same distillate to feed ratio.

Therefore it may be concluded that operating the column with a reboiler at constant heat duty should not have big consequences upon the limit cycle behaviour. Only one concern must be bared in mind. The reboiler duty must be such that the reflux is actually within the range which allows for limit cycle behaviour.
9.2.3 Results at Constant Utility Temperature

Again it is referred to Section 6.2, where it has been shown that the reflux has a big impact upon the bifurcation behaviour and may introduce a shift of the region or even the disappearance of limit cycles. As in the previous section, due to this influences here the reboiler specifications are chosen such that the resulting reflux would be approximately the same as in the reference model throughout the region of concern. This is done by specifying a utility temperature, which allows for a driving force of about 20 K and therefore is at 395 K. It has not been chosen to be higher for two reasons. First a very high utility temperature would cause a very high temperature at the reboiler walls and thus could introduce problems as the chemical degradation of the components in the mixture. This could introduce a subsequent change of the properties of the mixture and must be avoided in any case. On the other hand, the higher the temperature, the higher the cost for heating will be and thus in praxis it is a trade off between a utility temperature which is as low as possible and the size of the reboiler. And additional advantage when operating at the lowest possible utility temperature is that heat integration is more likely to be feasible and significant energy costs for complex processes may be saved.

Having specified the utility temperature only the heat transfer coefficient must be chosen such that it fulfills the requirements regarding a reflux flow rate, which should be in the range of the one specified in the original model.

Also in this case it was noticed that the reflux remained approximately constant throughout the the region of concern, thus along the upper branch of the temperature
bifurcation diagram, this can be seen in Figure 9.4. Therefore the change in the bifurcation behaviour was not expected to be significant. Again as in Section 7.5, this can be explained noticing that the composition in the reboiler does hardly change in the reboiler for that region. Therefore it can be concluded that neither temperature in the reboiler nor driving force nor boilup will change, which explains the constancy of the reflux along the upper branch of the temperature bifurcation diagram.

This is also found to be true and both bifurcation diagrams are depicted in Figure 9.5. As it can be seen, they hardly differ and also the Hopf bifurcation points occur at the same conditions.

Therefore it may be concluded that operating the column with a heat exchanger as reboiler at constant utility temperature and flow rate should not have big consequences upon the limit cycle behaviour. Only one concern must be bared in mind. The reboiler duty must be such, that the reflux is actually within the range which allows for limit cycle behaviour. In case of a heat exchanger this must considered already in the design stage. Since the range wherein a heat exchanger may be operated is restricted.

### 9.2.4 Conclusions

It was seen that the operating policy for the reboiler does not influence the bifurcation behaviour, which is mainly due to the fact that the reboiler composition remains more or less constant in the bifurcation region, and thus different operating policies have little influence as long the requirement is met, that the duty loaded to the reboiler allows for a certain reflux.

This restriction is however not too easy to fulfill, since in practice several assumptions underlying the CMO model used for these investigations do not hold in reality, although it is a good approximation. First of all the constant molar overflow assumption will not be met, which makes the exact calculation of the reflux from heat duties in the bottom almost impossible. Only estimates may be calculated.

The recommended set-up for the reboiler for an experiment would be a reboiler operated with heating candles. Heating candles usually allow for a wider range of operating conditions than heat exchangers. When laying out the reboiler it would be
9.3 Control of Flow Rates

When operating a real column, specifications cannot be done in terms of moles. This is due to the fact that moles are not a directly accessible measure. Therefore specifications will have to be made in mass or volumetric terms. Mass specifications are by far the easiest to measure and often specifications are made in mass terms.

In this section it shall be discussed what influences a mass based control will have upon limit cycle behaviour. This will include a short overview over different phenomena regarding the mass mole relationship.

9.3.1 Mass Measures

Here the relationship between mass flow rates and molar flow rates in mathematical terms shall be sketched shortly. To do so, first of all an average molar mass may be defined. Obviously this average molar mass depends on the composition and upon the molar masses of the components themselves.

\[
\sum_{i=1}^{n} x_i M_i = M_{av}\]  \hspace{1cm} (9.2)

Once the average molar mass is determined the conversion from one measure to the other is straight forward:

\[
L_{mass} = L_{molar} * M_{av}\]  \hspace{1cm} (9.3)
This conversion seems easy to perform and one might ask why it should be a problem to apply controls upon a molar basis. In practice moles are not a directly accessible measure. Usually mass or volumetric quantities are measured and the concentration has to be determined first to obtain molar quantities. Due to the fact that the online determination of concentration is slow and expensive, usually the directly accessible measures are used for control purposes.

9.3.2 Volumetric Measures

The relationship between volumetric measures and molar measures will now be sketched shortly. This relationship is based on the molar density of a mixture. For an ideal mixture, the average molar density may be calculated as follows.

$$\left( \sum_{i=1}^{n} \frac{x_i}{\rho_i} \right)^{-1} = \rho_{avg}$$

This average density may then be used for the conversion of volumetric measures into molar measures and vice versa.

$$L_{volume} = \frac{L_{molar}}{\rho_{avg}}$$

However, to develop this relationship already the assumption was made that there are no volumetric effects of mixing. Additionally to that highly nonlinear effect, it has always to be reared in mind that the molar density for a single component is highly nonlinear itself. Thus we have coupled highly nonlinear behaviour, whose prediction is very hard. There are functions which describe the molar density based on thermodynamics. However these functions are complex and involve many parameters.

Furthermore, to access molar measures again the concerns stated in the previous section (9.3.1) still hold. Therefore the measurements are volumetric they have to be used in that way, since their conversion into molar quantities is in practice not applicable.
CHAPTER 9. INFLUENCE OF SPECIFICATIONS ON LIMIT CYCLES

9.3.3 Mass Reflux and Bifurcation

To see what impacts a different specification of reflux might have, it was investigated how the reflux in mass terms would change throughout a bifurcation analysis performed at constant molar reflux. The resulting graph of this analysis is depicted in Figure 9.6. It can be seen that when specifying the reflux in molar terms the deviation of the mass reflux from constancy starts to become significant at the transition from the lower branch of the bifurcation to the middle branch. When talking about branches of the bifurcation diagram it is referred to a bifurcation diagram for the average temperature as depicted in Figure 9.1
However the lower and the middle branches are not of much concern for the limit cycle behaviour and therefore it is focused here onto the upper branch. It can be seen that the deviation induced by the middle branch is reversed by the upper branch. This means that also on the upper branch the mass reflux changes with constant molar reflux. The changes found are not too big though as can be seen in Figure 9.6. Nevertheless this behaviour could have an influence upon the limit cycle behaviour. Therefore the variation of the mass reflux during a dynamic simulation with constant molar reflux specification will be investigated in the next section.

9.4 Deviations of Mass Reflux upon Molar Control

The observations reported in the previous section are for steady state considerations only, in the case of limit cycle behaviour, the system is actually oscillating. This oscillating behaviour is illustrated in Figure 9.7 where a region of the composition space is drawn showing the trajectories of the distillate composition.

![Figure 9.7: The oscillations in the composition space for the Acetone Benzene n-Heptane System at a reflux of 48 and a distillate of 0.925](image)

This change in composition with time will have an influence upon a reflux in mass terms. As we saw the mass mole relationship is not constant on the upper branch of the bifurcation diagram, therefore this change will introduce a deviation of the reflux in mass terms from a constant one, if the molar reflux is kept constant. These deviations are expected to show oscillating behaviour as well. The results of this analysis can be found in Figure 9.8.

It can be seen that there are significant but relatively small deviations. Nevertheless, when the specifications for the model are now changed from molar to mass ones, this could have a significant influence upon the limit cycle behaviour. Fortunately this is not the case as it has been shown with detailed dynamic simulations in ASPEN Dynamics where actually all flow rates are specified in terms of mass. Results for such simulations may be retrieved in Section 7. The results presented in that section have all been retrieved with ASPEN Dynamics except where stated differently. It may therefore be concluded that the transition from constant molar flows to constant mass flows does not compromise the limit cycle behaviour.
Figure 9.8: Reflux mass flow rate which would correspond to a constant molar reflux flow rate of 48 at a distillate feed ratio of 0.925.
Chapter 10

Validation of the Column Design

All dynamic investigations so far have been performed with equilibrium based models. However, in reality equilibrium can never be reached in a distillation column. For that reason the whole column set-up determined so far must be validated and corrections must be determined. This can be done with a rate based model.

The rate based model used to check the column set-up and the effects observed for equilibrium based models was RateFrac which was presented in Section 2.4.2. However, with RateFrac only steady state simulations can be performed, since dynamic simulations for rate based models are still subject of actual research and are not yet available in commercial software packages. The validation of the column design was therefore only based on steady state criteria.

The main concern of the validation is to determine what dimensions would be needed for a packed column to perform the separation set-up. The results of the validation of the column set-up will now be presented in the next section.

10.1 Packed Column Dimensions

10.1.1 Layout in ASPEN RateFrac

Since this layout and this validation of the dimensions is made with regard to the experimental set-up, the original column for methanol-methylbutyrate-toluene has scaled to consume in the order of magnitude of 1 \( \frac{k_m}{h} \) of the experimental mixture as feed. The operating parameters used are listed in Table 10.1. With that set of operating parameters a column layout is developed to accomplish the separation task. The dimensions of the resulting column are listed in Table 10.2. Since RateFrac requires a set of quite specific specifications for the calculations they shall also be listed in that table. The thermodynamic properties used were the same as for the detailed dynamic analysis in Section 7.

The height of a theoretical stage is estimated to be within 5 to 10 cm. When looking at those specifications, it can be seen that this column should meet the requirements regarding its size and could actually be realized. However, there are certain aspects regarding the results obtained whose influences are not yet known. They will be discussed in the next section.
Table 10.1: Operating conditions and streams for column set-up

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>reflux to feed ratio</td>
<td>0.2</td>
</tr>
<tr>
<td>distillate to feed ratio</td>
<td>0.955</td>
</tr>
<tr>
<td>feed flow rate [kmol/h]</td>
<td>0.010</td>
</tr>
<tr>
<td>feed flow rate [kg/h]</td>
<td>0.401</td>
</tr>
<tr>
<td>feed composition methanol (mole fraction)</td>
<td>0.8671</td>
</tr>
<tr>
<td>feed composition methylbutyrate (mole fraction)</td>
<td>0.0050</td>
</tr>
<tr>
<td>feed composition toluene (mole fraction)</td>
<td>0.1279</td>
</tr>
</tbody>
</table>

Table 10.2: Column set up in ASPEN RateFrac

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>number of segments</td>
<td>220</td>
</tr>
<tr>
<td>inlet above segment</td>
<td>175</td>
</tr>
<tr>
<td>equilibrium segments</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>220</td>
</tr>
<tr>
<td>height per segment [m]</td>
<td>0.015</td>
</tr>
<tr>
<td>column diameter [m]</td>
<td>0.100</td>
</tr>
<tr>
<td>total column height [m]</td>
<td>3.300</td>
</tr>
<tr>
<td>condenser pressure [atm]</td>
<td>1</td>
</tr>
<tr>
<td>column pressure drop [Pa]</td>
<td>20000</td>
</tr>
<tr>
<td>reboiler type</td>
<td>kettle</td>
</tr>
<tr>
<td>condenser type</td>
<td>total</td>
</tr>
<tr>
<td>packing</td>
<td>structured</td>
</tr>
<tr>
<td>packing producer</td>
<td>sulzer</td>
</tr>
<tr>
<td>packing name</td>
<td>CY Metal</td>
</tr>
</tbody>
</table>

10.1.2 Concerns

When looking at the column profiles obtained with the simulations set up as described in the previous section one notices an unexpected behaviour. In Figure 10.1 the profiles for the equilibrium based simulations with ASPEN RadFrac are compared with the rate based results obtained with ASPEN RateFrac. It can clearly be seen, that the profile for the rate based model is bent far more outwards. This is unexpected, since when introducing overall efficiency expressions (same Murphree efficiency for all components), profiles tend to be bent less.

Up to now it is not known how this effect would influence the limit cycle behaviour. However it can be noticed that the column profile is still of unstable nature according the criteria defined in the dynamic analysis presented in (Dorn 2000). In fact it is non monotonous in all three components.

When looking at the column profiles only superficially, it seems as if they would evolve something like degenerated multiplicities as discussed in (Bekiaris et al. 1993) but when looking a little closer to the ending points of the column profiles depicted in the Figures 10.2 and 10.3 it can be seen that this is actually not true, furthermore the degenerate multiplicities reported in (Bekiaris et al. 1993) where restricted to column profiles having their ending points in nodes only and to the $\infty/\infty$-case.
10.2 Validation of the Holdup

Now that the height of a theoretical stage is approximately known, it is crucial to know how big the actual holdup on a theoretical stage is. As it has been seen in Section 7.2, this holdup would strongly influence the period of oscillation.

This validation has been performed with Sulpak again. Sulpak has already been presented in Section 7.3.2 to qualitatively verify the behaviour of holdup in dependence on reflux flow rate for Sulzer structured packings. However this time the interest has far more a quantitative nature. Since it would be liked to calculate the actual characteristic time of exchange of a theoretical stage for the column set-up presented in last section.

In order to be able to calculate the holdup in a column Sulpak needs physical properties of the mixture. The physical properties required by Sulpak are the viscosities, the mass density and the surface tension. Additionaly Sulpak needs information about the column geometry, the packing and the flow rates. The latter specifications were already done when validating the column design with ASPEN RateFrac in last section. Thus only the physical properties had to be specified.

The physical properties required by Sulpak cannot be retrieved from standard databases, because the system methanol-methylbutyrate-toluene is quite special. Furthermore the conditions wherein the properties are required is around the boiling point of the different mixtures, which makes it even harder to retrieve appropriate data. Therefore estimates must be chosen. This choice of estimates has been done in a broad range in order to cover all eventual effects.

Typical values for the liquid viscosity of organic substances which are close to the boiling point are usually between 1 and 2 cP. For the gas viscosities close to the dew point typical values were found to be between 0.005 and 0.01 cP.
The density of organic substances is usually around 800 $\frac{kg}{m^3}$. In order to cover all eventualities values between 600 and 900 $\frac{kg}{m^3}$ have been considered.

Surface tensions for organic components are usually between 0.01 and 0.025 $\frac{N}{m}$.

While a rise in surface tension and in viscosity tends to increase the liquid holdup in a column, a rise in liquid density tends to decrease the liquid holdup. Therefore a maximal holdup is achieved at maximal surface tension and viscosity while the density is minimal. For the minimal holdup it’s vice versa.

Performing calculations for both cases, thus a best and a worst case, the volume fraction occupied by liquid is always between 5 and 10%. 10% are only exceeded if the fluxes are increased significantly.

Assuming a height of a theoretical stage to be 10 cm, the liquid holdup for one theoretical stage may be calculated and scaled with the reflux flow rate in order to obtain the characteristic time for a theoretical stage. Again the values taken always assume the "worst” case. The characteristic time is about 0.001 h. This corresponds to a value at the very lower end in the Figure 7.4. Therefore a column set-up as presented before should allow for periods of oscillations close to the lower limit achievable.
Figure 10.3: Comparison of the column profiles for ASPEN RateFrac and ASPEN Radfrac towards the bottom of the column
Chapter 11

Conclusions and Recommendations

In this chapter a conclusion is drawn from the results presented in this work and some recommendations for the experimental setup are presented. Whereupon a short overview will be given concerning the aspects which still need validation before an experimental setup.

As it could be seen in Chapter 10 there are still uncertainties regarding the column set-up and the feasibility of a column which, will actually evolve limit cycle behaviour. Nevertheless the author is quite optimistic that the uncertainties will not influence the behaviour, since no argument could be found which indicated that limit cycle behaviour could be compromised.

Due to that optimism a set-up shall be recommended here which should evolve limit cycle behaviour. The setup is summarized in Table 11.1. As it can be seen the set-up is quite close to the one presented in Section 10. The only differences regard the column height and the column packing. The column height was increased due to the findings in the Sections 7.4 and 7.5, which indicated that a higher number of stages would be favorable for any experimental setup. The change in the packing is due to the fact that in ASPEN Plus there was only data for technical packing available. The packing which will be used for the experimental set-up is a laboratory packing though and should allow for a shorter height of a theoretical stage and thus should allow for additional stages as well and a lower characteristic time of the column dynamics.

The desire for additional stages is not only based on the fact that it might be favorable for the measurements in terms of experiment duration and stability, but there are still uncertainties how exact the correlations used for mass transfer in ASPEN RateFrac actually represent reality. In fact those correlations could easily bare errors of 10% and more. But this is not the only uncertainty, others still have to be validated. They are presented in the next section with some recommendations regarding their validation.

11.1 Missing Validations

11.1.1 Column Profiles

As announced in the previous section the influences of the difference in the column profiles is still not clear. Thus it would be favorable to validate that those differences
Table 11.1: Recommended experimental setup

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>reflux to feed ratio</td>
<td>0.2</td>
</tr>
<tr>
<td>distillate to feed ratio</td>
<td>0.955</td>
</tr>
<tr>
<td>feed flow rate [kmol/h]</td>
<td>0.010</td>
</tr>
<tr>
<td>feed flow rate [kmol/h]</td>
<td>0.401</td>
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<tr>
<td>feed composition methanol (mole fraction)</td>
<td>0.8671</td>
</tr>
<tr>
<td>feed composition methylbutyrate (mole fraction)</td>
<td>0.0050</td>
</tr>
<tr>
<td>feed composition toluene (mole fraction)</td>
<td>0.1279</td>
</tr>
<tr>
<td>column diameter [m]</td>
<td>0.100</td>
</tr>
<tr>
<td>total column height [m]</td>
<td>4.000</td>
</tr>
<tr>
<td>condenser pressure [atm]</td>
<td>1</td>
</tr>
<tr>
<td>reboiler type</td>
<td>candle</td>
</tr>
<tr>
<td>condenser type</td>
<td>total</td>
</tr>
<tr>
<td>packing</td>
<td>structured</td>
</tr>
<tr>
<td>packing producer</td>
<td>Sulzer</td>
</tr>
<tr>
<td>packing type</td>
<td>DX</td>
</tr>
</tbody>
</table>

do not have an awkward influence onto the limit cycle behaviour. Since a dynamic simulation cannot be performed with a rate based model, it is recommended to performed this validation with a equilibrium based model, which is extended through component efficiency expressions in order to reproduce the column profile observed with the rate based model.

11.1.2 Feed Concentration

In (Dorn 2000) and in Section 6.1.2 it was reported that if the feed concentration is moved into the Ω-region for systems of the 001 class there will arise systems which report one Hopf bifurcation only. Those systems will have unstable steady states which evolve limit cycle behaviour only for distillate to feed ratios close to unity.

It might be favorable to perform an experiment for a system which can evolve limit cycle behaviour only. Since such a system could not drop onto a second stable steady state and thus might be more convenient for an experimental set-up.
Bibliography


Appendix A

Thermodynamic Property Models

During this work the accuracy of thermodynamic data has been shown to be very important. In order to allow for reproduction of the results obtained, this data shall be presented in the next chapter of the Appendix.

In this part the underlying thermodynamic property models are shortly presented. This presentation will not go into detail and the reader is referred to specific literature for further information.

A.1 Antoine

The Antoine Model is an empirical expression for the vapor pressure of a pure component \( i \). In combination with the Wilson model, described later, the Antoine expression allows to determine liquid fugacities in good approximation. The coefficients of the Antoine model have to be found by fitting them to experimental data.

Because of its simplicity and accuracy this model is widely used for calculations of vapor liquid equilibria. The equation representing the Antoine model is given below:

\[
\ln \left( \frac{\theta_i}{\theta_i^0} \right) = A_i + \frac{B_i}{T + C_i} \quad (A.1)
\]

Where the Temperature \( T \) is usually measured in Kelvin and the vapor pressure would be given in Pascal. However in literature many different forms of this expression can be found and therefore the coefficients, its units and its signs have to be checked carefully.

A.2 Wilson

With the Wilson model liquid activity coefficients may be calculated. As a simple model with a good capability to cope with highly non ideal systems, especially alcohol-water systems, it is very often the first choice for modeling purposes.

Unfortunately this model cannot be used for liquid liquid equilibrium calculations. This has however not been a problem since this work deals explicitly with homogeneous azeotropic distillation. Nevertheless, if there exists an uncertainty, whether a
system exhibits a liquid liquid phase split this has to be checked with other property methods as for example UNIQUAC or UNIFAC.

The main equation for the Wilson model is the definition of the activity coefficient as:

\[
\ln \gamma_i = 1 - \ln \left( \sum_j A_{ij} x_j \right) - \sum_j \frac{A_{ij} x_j}{\sum_k A_{jk} x_k} \tag{A.2}
\]

Where the following definition applies:

\[
\ln A_{ij} = a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln T + d_{ij} T \tag{A.3}
\]

The Wilson model must be used carefully, since the interaction coefficients are not symmetric with respect to both components. So we have to note that:

\[
a_{ij} \neq a_{ji} \tag{A.4}
\]
\[
b_{ij} \neq b_{ji} \tag{A.5}
\]
\[
c_{ij} \neq c_{ji} \tag{A.6}
\]
\[
d_{ij} \neq d_{ji} \tag{A.7}
\]

The binary parameters \( a_{ij}, b_{ij}, c_{ij} \) and \( d_{ij} \) must be determined from vapor liquid equilibrium data regression, but can also be retrieved from predictive property methods such as UNIFAC. The latter proceeding is not recommended, though. Additional information regarding the Wilson model can be retrieved in (Wilson, 1964).

### A.3 UNIQUAC

Also the UNIQUAC model can be used to calculate liquid activity coefficients. As the Wilson model described before it is a powerful model to model highly non-ideal chemical systems. It may be used for vapor liquid and liquid liquid equilibrium applications.

The main equation in the UNIQUAC model for us is again the definition of the activity coefficient as:

\[
\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\Theta_i}{\Phi_i} - q_i' \ln t_i' - \frac{q_i' \sum_j \Theta_j' t_{ij}}{t_{ij}} + l_i + q_i' \sum_j x_j l_j \tag{A.8}
\]

Where the surface fraction and the residual surface fraction are defined as:

\[
\Theta_i = \frac{q_i x_i}{\sum_k q_k x_k} \tag{A.9}
\]
\[
\Theta_i' = \frac{q_i' x_i}{\sum_k q_k' x_k} \tag{A.10}
\]

The segment fraction is defined as:

\[
\Phi_i = \frac{r_i x_i}{\sum_k r_k x_k} \tag{A.11}
\]

The parameters \( l_i \) and \( t_i' \) may be calculated as follows:

\[
l_i = \frac{z}{2} (r_i - q_i) + 1 - r_i \tag{A.12}
\]
\[ t'_i = \sum_k \Theta'_k \tau_{ki} \]  
(A.13)

Where \( r_i \) and \( q_i \) are component specific parameters. The coordination number \( z \) is usually set to a value of 10 which is accurate enough for most purposes. The interaction is accounted for by the interaction parameter \( \tau_{ij} \).

\[ \tau_{ij} = \exp \left( a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln T + d_{ij}T \right) \]  
(A.14)

Again, the interaction parameters are not symmetric and must be handled with care:

\[ a_{ij} \neq a_{ji} \]  
(A.15)

\[ b_{ij} \neq b_{ji} \]  
(A.16)

\[ c_{ij} \neq c_{ji} \]  
(A.17)

\[ d_{ij} \neq d_{ji} \]  
(A.18)

The binary parameters can be determined from VLE and/or LLE data regression. Additional information regarding this model can be from (Abrams and Prausnitz, 1975), (Bondi, 1960) or (Simonetty et al., 1982).

### A.4 UNIFAC

The UNIFAC model can be used to calculate liquid activity coefficients but it can also be used to estimate according coefficients for the UNIQUAC model. This predictive feature of the UNIFAC model is based on its nature as a group-contribution model and makes it a powerful tool for many purposes.

The equation for the original UNIFAC liquid activity coefficient model is made up of a combinatorial and residual term:

\[ \ln \gamma = \ln \gamma_i^c + \ln \gamma_i^r \]  
(A.19)

Where the combinatorial term is equal to:

\[ \ln \gamma_i^c = \ln \frac{\Phi_i}{x_i} + 1 - \frac{Z}{2} \left( \ln \frac{\Phi_i}{\Theta_i} + 1 - \frac{\Phi_i}{\Theta_i} \right) \]  
(A.20)

here the molecular volume and surface fractions are:

\[ \Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \]  
(A.21)

and

\[ \Theta_i = \frac{x_i \frac{z}{2} q_i}{\sum_j x_j \frac{z}{2} q_j} \]  
(A.22)

The summation is over all components \( n_c \) in the mixture. The coordination number \( z \) is set to 10. The parameters \( r_i \) and \( q_i \) are calculated from the group volume and the area parameters:

\[ r_i = \sum_k n_k v_{ki} R_k \]  
(A.23)
In the last two equations \( \nu_{ki} \) is the number of groups of type \( k \) in molecule \( i \), and \( n_g \) is the number of groups in the mixture. The residual term is:

\[
\ln \gamma_i' = \sum_k \nu_{ki} \left[ \ln \Gamma_k - \ln \Gamma_i^k \right]
\]  

(A.25)

\( \Gamma_k \) is the activity coefficient of a group at mixture composition, and \( \Gamma_i^k \) is the activity coefficient of group \( k \) in a mixture of groups corresponding to pure \( i \). The parameters \( \Gamma_k \) and \( \Gamma_i^k \) are defined by:

\[
\ln \Gamma_k = Q_k \left( 1 - \ln \sum_m \Theta_m \tau_{mk} - \sum_m \frac{\Theta_m \tau_{km}}{\sum_n \Theta_n \tau_{nm}} \right)
\]  

(A.26)

With

\[
\Theta_k = \frac{X_k \gamma_k \bar{z} Q_k}{\sum_m X_m \gamma_m \bar{z} Q_m}
\]  

(A.27)

And:

\[
\tau_{mn} = \exp \left( -\frac{b_{mn}}{T} \right)
\]  

(A.28)

The parameter \( X_k \) is the group mole fraction of group \( k \) in the liquid:

\[
X_k = \frac{\sum_{j} \nu_{kj} x_j}{\sum_{j} \sum_{m} \nu_{mj} x_j}
\]  

(A.29)

Additional information regarding the UNIFAC model can be retrieved from (Fredenslund et al., 1975), (Fredenslund et al., 1977) or (Hansen et al., 1991).

### A.5 Thermodynamics in ASPEN PLUS

ASPEN Plus has a large number of built-in binary parameters for the Wilson model as well as parameters for the UNIQUAC model. Most of these parameters have been regressed using either vapor liquid equilibrium data or liquid liquid equilibrium data (only UNIQUAC) from the Dortmund Databank. The binary parameters were regressed using the ideal gas, Redlich Kwong, and Hayden-O’Connell equations of state. Therefore the databank of ASPEN Plus is a very powerful and reliable source for thermodynamic data.

For the UNIFAC model ASPEN Plus has stored all published group parameters and group binary parameters according to its producer.
Appendix B

Thermodynamic Parameters

B.1 Acetone-Benzene-\(n\)-Heptane

The thermodynamic parameters are taken from (Güttinger and Morari, 1996). The Antoine coefficients are from Thermopack, which are thermodynamic subroutines provided by Prof. M. F. Doherty and J. Knapp (University of Massachusetts, Amherst).

The Wilson parameters for the binary acetone-benzene are from ASPEN Plus, the other binaries are from Thermopack.

Table B.1: Antoine parameters

<table>
<thead>
<tr>
<th></th>
<th>Acetone</th>
<th>Benzene</th>
<th>(n)-Heptane</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_i)</td>
<td>21.3099</td>
<td>20.7936</td>
<td>20.7664</td>
</tr>
<tr>
<td>(B_i)</td>
<td>-2801.53</td>
<td>-2788.51</td>
<td>-2911.32</td>
</tr>
<tr>
<td>(C_i)</td>
<td>-42.875</td>
<td>-52.36</td>
<td>-56.514</td>
</tr>
</tbody>
</table>

Table B.2: Wilson coefficients, temperature dependent

\(A_{ij}\) values:

<table>
<thead>
<tr>
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<th>Acetone</th>
<th>Benzene</th>
<th>(n)-Heptane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>0.0</td>
<td>0.1881</td>
<td>6.6884</td>
</tr>
<tr>
<td>Benzene</td>
<td>-0.1885</td>
<td>0.0</td>
<td>0.6004</td>
</tr>
<tr>
<td>(n)-Heptane</td>
<td>-0.6889</td>
<td>-0.0004</td>
<td>0.0</td>
</tr>
</tbody>
</table>

\(B_{ij}\) values:

<table>
<thead>
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<th>Acetone</th>
<th>Benzene</th>
<th>(n)-Heptane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
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<td>-847.5111</td>
</tr>
<tr>
<td>Benzene</td>
<td>91.8489</td>
<td>0.0</td>
<td>-75.4771</td>
</tr>
<tr>
<td>(n)-Heptane</td>
<td>-227.9996</td>
<td>-117.2218</td>
<td>0.0</td>
</tr>
</tbody>
</table>
### B.2 Methanol-Methylbutyrate-Toluene

The thermodynamic parameters for this mixture are taken from (Güttinger et al., 1997). The Antoine coefficients are from Thermopack.

For the Wilson model, the coefficients for the binary methanol-toluene are taken from (Gmehling and Onken, 1977). For the other two binaries, they have been re-regressed with the ASPEN Plus properties estimation option from data generated with UNIFAC with Dortmund corrections.

During simulation also UNIQUAC parameters have been used. For this model ASPEN Plus 10.2 provides experimental data for the binary methanol-toluene, while the other binaries have been estimated through UNIFAC. (without Dortmund corrections) This data is not explicitly listed here.

#### Table B.4: Antoine coefficients

<table>
<thead>
<tr>
<th></th>
<th>Methanol</th>
<th>Methylbutyrate</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_i$</td>
<td>23.4832</td>
<td>20.511</td>
<td>20.9064</td>
</tr>
<tr>
<td>$B_i$</td>
<td>-3634.01</td>
<td>-2664.3</td>
<td>-3096.52</td>
</tr>
<tr>
<td>$C_i$</td>
<td>-33.7680</td>
<td>-79.483</td>
<td>-53.668</td>
</tr>
</tbody>
</table>

#### Table B.5: Wilson coefficients

<table>
<thead>
<tr>
<th></th>
<th>Methanol</th>
<th>Methylbutyrate</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{ij}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>0.0</td>
<td>0.7411</td>
<td>0.9645</td>
</tr>
<tr>
<td>Methylbutyrate</td>
<td>-1.025</td>
<td>0.0</td>
<td>-1.435</td>
</tr>
<tr>
<td>Toluene</td>
<td>-0.9645</td>
<td>2.747</td>
<td>0.0</td>
</tr>
</tbody>
</table>

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{ij}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>0.0</td>
<td>-477.0</td>
<td>-903.1024</td>
</tr>
<tr>
<td>Methylbutyrate</td>
<td>72.78</td>
<td>0.0</td>
<td>768.2</td>
</tr>
<tr>
<td>Toluene</td>
<td>-140.9995</td>
<td>-1419.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
B.3 Ethanol-Triethylamine-Butylethylether

The thermodynamic parameters are taken from two sources. The Antoine coefficients are from NIST, National Laboratory of Standards and Technology, an agency of the United States’ Commerce Department. The database can be found at the webpage: http://webbook.nist.gov/chemistry/

The UNIQUAC parameters for the binary ethanol-triethylamine are experimental data from ASPEN Plus, the other binaries are estimates based on the UNIFAC model.

Table B.6: Antoine coefficients

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>Triethylamine</th>
<th>Butylethylether</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_i$</td>
<td>23.594059</td>
<td>18.383103</td>
<td>20.867339</td>
</tr>
<tr>
<td>$B_i$</td>
<td>-3681.0806</td>
<td>-1602.1709</td>
<td>-2883.9533</td>
</tr>
<tr>
<td>$C_i$</td>
<td>-46.424</td>
<td>-128.271</td>
<td>-56.685</td>
</tr>
</tbody>
</table>

Table B.7: Wilson coefficients from ASPEN

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>Triethylamine</th>
<th>Butylethylether</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{ij}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Butylethylether</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$B_{ij}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.0</td>
<td>-287.9032</td>
<td>342.508817</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>68.941</td>
<td>0.0</td>
<td>-118.608622</td>
</tr>
<tr>
<td>Butylethylether</td>
<td>-232.792211</td>
<td>87.671317</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table B.8: Estimated temperature independent Wilson coefficients based on ASPEN at 360 K

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>Triethylamine</th>
<th>Butylethylether</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{ij}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.0</td>
<td>0.44945</td>
<td>0.38619</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>1.21107</td>
<td>1.0</td>
<td>0.71931</td>
</tr>
<tr>
<td>Butylethylether</td>
<td>0.52380</td>
<td>1.27575</td>
<td>1.0</td>
</tr>
</tbody>
</table>
B.4 Isobutanol-Pyridine-Formic Acid

The thermodynamic parameters are taken from two sources. The Antoine coefficients are from NIST. The database can be found at http://webbook.nist.gov/chemistry/

All Wilson parameters used have been estimates with the UNIFAC model in AS-PEN Plus.

<table>
<thead>
<tr>
<th>Table B.9: Antoine coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>$A_i$</td>
</tr>
<tr>
<td>$B_i$</td>
</tr>
<tr>
<td>$C_i$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table B.10: Wilson coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>$A_{ij}$</td>
</tr>
<tr>
<td>Isobutanol</td>
</tr>
<tr>
<td>Pyridine</td>
</tr>
<tr>
<td>Formic Acid</td>
</tr>
</tbody>
</table>

|                                | $B_{ij}$   |
|                                |            |
| Isobutanol         | 0.0        | -133.507  | -889.316492 |
| Pyridine           | -98.2536   | 0.0       | 356.200934  |
| Formic Acid        | 97.359793  | 327.375661| 0.0         |