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Thermodynamic Analysis of the Sequencing, Feed Tray and Interstage Heat Exchanger Location in Multi Component Distillation

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Abstract

The aim of this final thesis is the application and comparison of several thermodynamic analysis methods for three different design variables in multi component distillation. The simulations of the distillation columns were mainly done with a program in C based on the method of tray-to-tray calculation. The equilibria on the trays were calculated with a new and fast concept that consisted of the combination of a data grid and an interpolation technique. The results of the program were accurate but the number of components was limited to three due to memory limitations of the software.

First, the optimal sequence of distillation columns is analysed. A new approach is used that is based on the sum of a performance determining variable of each sequence. The sequence which has the minimum value for this sum should be the most optimal one. It was already known that the vapour load was useful for this variable. But this analysis has proved that a simple equation based on exergy loss gives better results. The contribution of this analysis is that after a simple exergy calculation only two or three possible sequences are left for a more rigorous analysis and therefore much time is saved.

The second design variable is the location of the feed tray. Besides the reflux ratio, the feed tray determines the number of trays in a distillation column. It is assumed that if the effects of mixing on the feed tray are minimum, the feed tray location is optimal. It is observed that the entropy production rate due to mixing on the feed tray predicted the optimal feed tray location on the edge of acceptance, but better than exergy loss due to same mixing. This is surprising because the predictability should be approximately equal. This result is however very dependant on how the mixing and thermodynamic model are defined. The temperature difference between the two flows which are mixed did not succeed at all to predict the optimal feed tray location. 2

Finally, the location of the interstage heat exchangers is analysed with exergy in combination with the principle of equipartition of forces. According to this principle minimum exergy loss is obtained when the forces are equipartitioned over the whole column. Interstage heat exchangers are a theoretically proved method for reducing the exergy loss and they also affect the course of the driving forces. So, interstage heat exchangers at the right location can make the forces more equipartitioned. Varying the position of the heat exchangers, it has been observed that the deviation of the key force from the equipartitioned course is proportional to the total exergy loss. So, this is a practical application of the principle and it is therefore a step in the development towards a real engineering tool. This analysis has also affirmed the consideration of a distillation column as a dissipative structure. 3

The main conclusion is that the aim is successfully pursued. It is still possible to improve a relative old process like distillation with modern thermodynamic analysis tools like exergy and the equipartition of forces. The main recommendation is to develop the principle of equipartition of forces further with other processes in the chemical industry. But this work can also be a start for investigation of the flexibility and maximum output of a distillation column.

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1. Introduction

1.1 Aim

The aim of this final thesis is the application and comparison of several thermodynamic analysis methods for the sequencing of columns, the feed tray location and the location of interstage heat exchangers in multi component distillation. The analysis methods are for the sequencing exergy and vapour load. The feed tray will be analysed with exergy, entropy and temperature difference. For the interstage heat exchangers again exergy will be used but also the application of the principle of equipartition of forces is pursued.

1.2 Scope

Distillation is the most common and reliable separation method currently used in the chemical and refinery industry. But it is also a large energy consumer and it is therefore not surprising that 3 % of the total energy demand in the United States is used for distillation. As in recent year several aims have been made in the chemical and refinery industry with respect to energy saving, distillation has to contribute also to these reductions. A lot of research already has been done on this reduction of the energy demand of distillation. The most promising results are obtained by inventing new designs. For example the additions of a heatpump or vapour compression have proved to be very good energy saving measures.

In this project three design variables will be analysed and where possible optimised. The first variable is the sequencing of the columns that separate a multi component mixture into its pure fractions. The second variable is the number of trays and the location of the feed tray in a single column. And the last is the location of heat exchangers between two trays. With changing these variables, the designs also change and therefore a distinction has to be made between the alternative designs, because only one design leads to the optimal distillation columns. And it is this distinction that is to be solved with the thermodynamic tools.

For analyses of such energy consuming processes, several thermodynamic tools are available. Exergy analysis is one of the most powerful optimisation tools because it is the only tool that combines the first and second law of thermodynamics incorporating the interactions with the environment. In this thesis, the three variables will be analysed with this exergy and these analyses will be compared with other thermodynamic tools.

Another thermodynamic tool is the principle of equipartition of forces. According to this principle, the optimal design of a process is obtained when the driving forces are equally distributed over the transport path. As this principle is based on irreversible thermodynamics, it is not a real engineering tool. This thesis will try to make a bridge between the type of findings from irreversible thermodynamics and the typical engineering tool of exergy analysis. This attempt will be made in the chapter 6, which deals with interstage heat exchangers.

1.3 Outline of this report

The first chapter is this introduction. The second chapter will discuss how distillation is defined and analysed in this thesis and which assumptions are made. Also a short introduction to exergy analysis will be given, which is one of the most powerful thermodynamic analysis methods currently available. This tool will be discussed here because it is used for all the three different variables, which are analysed in this thesis. The third chapter describes the program written in the language C. This program is the basis for the calculations of the simulations for the feed tray and interstage heat exchanger analyses. Chapter four gives an extension of a new way to determine the optimal sequence of distillation columns. This new way is based on the minimisation of the sum of a performance determining variable. Of course exergy will be used as this variable. In chapter five the rigorous calculation of the number of trays and the optimal feed tray will be discussed. The main part is the minimisation of the effects due to the entering of the feed using exergy and entropy. Also a comparison will be made with common shortcut methods for calculating these variables. The sixth chapter will present a discussion about the location of the interstage heat exchangers. Here irreversible thermodynamics and the principle of equipartition of forces will also be used as an analysis tool. The last chapter will give the conclusions and recommendations.

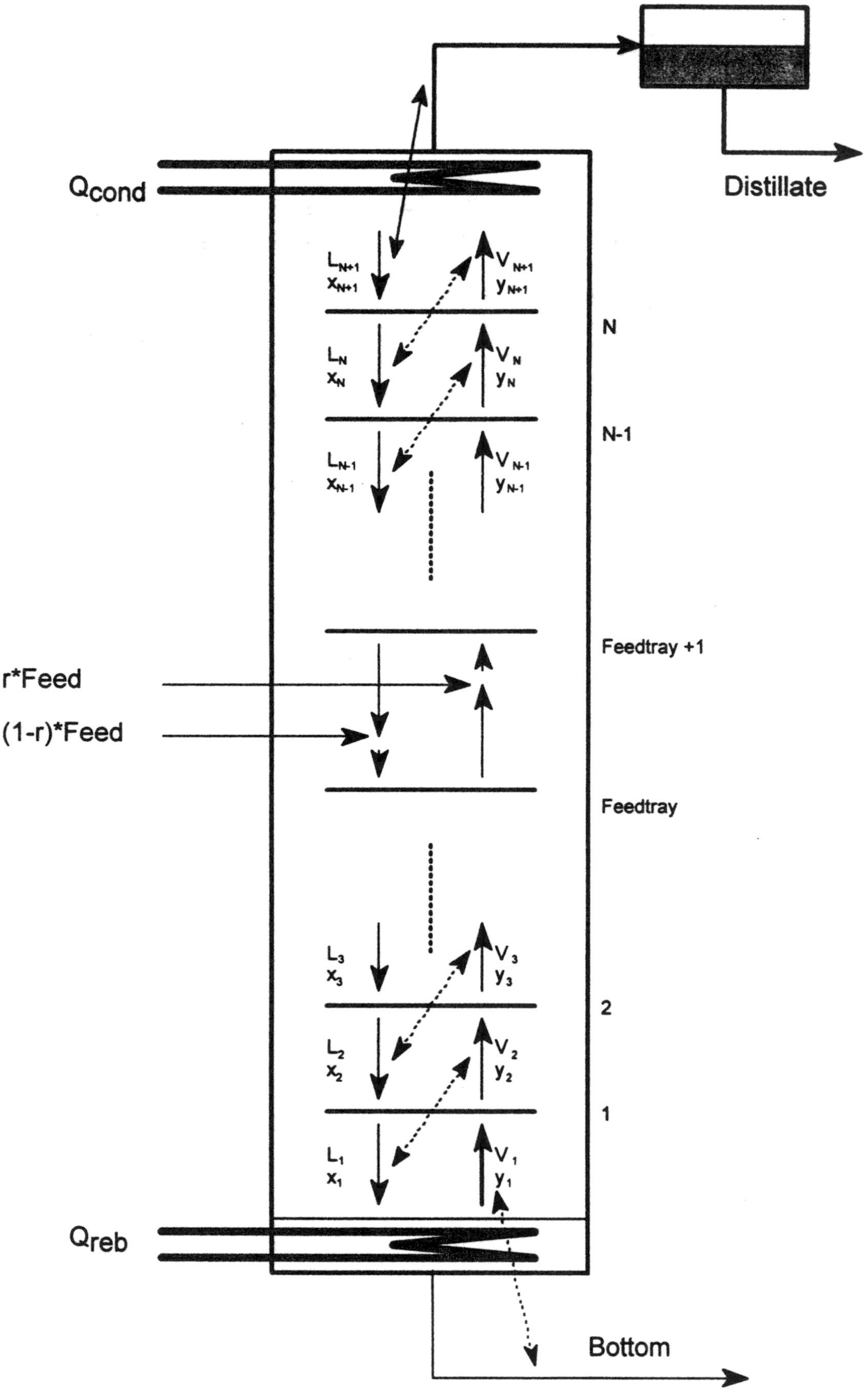

Figure 2.1 : Scheme of a distillation column

2. Aspects of Distillation

2.1 Introduction

This chapter will give an overview of the different aspects of how distillation is analysed in this final thesis. So the terminology, assumptions, a model and the thermodynamic analysis tool called exergy analysis will be treated.

The basis of the separation with distillation is the difference in boiling temperature of two components. The definition of multi component distillation is the distillation of mixtures with three or more components. The largest part of the fundamental research done on distillation is only valid for two components (binary distillation). This type of distillation is also analysed with exergy at least three times by Strijk[20], Ognisty[14] and Fitzmorris[4]. But the approach of multi component distillation with exergy is still in its infancy. The main problem of multi component analysis is that the number of degrees of freedom increases together with the number of components. So, the number of assumptions and/or the number of equations must also increase and the aim is to investigate in how far these extra degrees of freedom and equations influence the total behaviour.

2.2 Definition of the terms used in distillation

A schematic representation of a distillation column is given in figure 2.1. The numbering of the flows and mole fractions is taken from the reboiler until the top upwards and the flows and mole fractions under the same tray have the same number. This is very important for the derivation and understanding of the equations in this report! For comprehending the analyses done in this thesis, a short explanation of the terms used in distillation is given:

Feed
The feed is the stream that enters the column above the so called feed tray. In these calculations in this thesis, the concentrations and the fraction vapour(r) can be varied. If a 100% liquid feed is chosen the feed will be a boiling liquid and if a 100% vapour feed is chosen, it is a condensing vapour. Bu all the calculations done in this thesis are with a 100% liquid. The feed is always given in mole/s.

Distillate/Bottom
The distillate is the product stream coming out of the top of the column, containing the components with high volatilities. The bottom is the product stream coming out of the bottom of the column and it contains the least volatile components.

Reboiler
The reboiler is a heat exchanger at the bottom of the column and it evaporates a part of the liquid that comes from the lowest tray (L_1). The rest of the liquid flow is the

bottom product stream (B). So, energy goes in to create a rising vapour stream (V_1), which is in equilibrium with the bottom. The energy is usually supplied by steam.

Condenser

The condenser is a heat exchanger at the top of the column and it condenses a part of the rising vapour from the highest tray (V_N). The rest of this vapour is condensed totally in this model and is the top product stream(D). For this condensation process heat is removed, which is usually done with cooling water.

Tray

On the trays the actual separation takes place. On each tray a down coming liquid is brought into equilibrium with a rising vapour with different mole fractions and temperatures (shown by the arrows in figure 2.1). Due to this equilibrium the mole fractions in the liquid and vapour change so that the driving forces decrease by mass and energy transport. The changed vapour is brought again in contact with a liquid flow on a tray higher and the changed liquid with a vapour on a tray lower.

Heavy key / Light key

In a multi component mixture the heaviest component of which the largest part comes into the distillate is called the light key. And the lightest component of which the largest part comes into the bottom is called the heavy key. The light and heavy key have always two consecutive volatilities in the row of the volatilities of all components in the mixture. So, the actual separation is done between these two components.

Heavy non-key / Light non-key

Non-key components are the components which nearly do not take part in the actual separation. The heavy non-key components have a lower volatility than the heavy key and the light non-key components have a higher volatility than the heavy key.

Reflux ratio

The reflux ratio is usually the ratio between the flow that is returned by the reboiler or condenser into the column and the corresponding product flow (bottom or distillate). It is the most important variable in the distillation column because it determines the number of trays and energy demand. The actual reflux ratio is the ratio that is actually used and the minimum reflux ratio is the theoretically possible lowest reflux ratio. This minimum reflux ratio is theoretical because it requires an infinite number of trays. The actual reflux ratio is calculated by the multiplication of the minimum reflux ratio and a factor. Also, an internal reflux ratio can be defined. This is the ratio between the vapour and liquid flow below the same tray.

Stripping section / Rectifying section

The portion of the tower below the feed is called the stripping section and serves primarily to remove or strip the light key component from the down coming liquid. And the part above the feed is called the rectifying section because it primarily removes the heavier component from the rising vapour.

Equimolar overflow

The assumption of equimolar overflow states that the condensation of the heavy key is compensated by an equal evaporation of the light key on each tray. The effect of this assumption is that the flows are constant i.e. the internal reflux ratio is constant. This assumption simplifies the calculations a lot. But it could not be used in this project because the energy balances are not correct (see also Wesseling[24], page 50). And it would make an energy and exergy analysis impossible.

2.3 Distillation as a dissipative Structure

According to De Swaan Arons [2] a distillation column can be considered as a dissipative structure. This means that the total amount of work is separated into two contributions: one to sustain the "structure" of the column and one to actually produce the separated products. The "structure" of the column can be seen as the maintenance of the rising vapour and down coming liquid flows and can be changed by altering the design or settings. The part of the work for the separation can only be changed by altering the recoveries. As the recoveries are fixed in process design situations, the only part that is left for minimisation is the part of the "structure". So, all the optimisations and efficiency improvements can only be done by decreasing the losses due to the "structure". This discussion will be become important in the chapter about the interstage heat exchangers (chapter 6).

2.4 Assumptions

For the calculations for the three variables several assumptions are made. These assumptions are necessary in order to keep the project surveyable. The assumptions differ for each variable but the assumptions that are valid for all three variables are:

1. On all the trays equilibrium is assumed. So, no tray efficiencies are applied and the results are always the number of theoretical trays. Addition of tray efficiencies does not create much more insight and it makes the calculations unnecessarily complex.
2. There is no pressure drop over the column. Again the motivation for this assumption is that it does not create much more insight and make the calculations unnecessarily complex. Certainly the equilibrium calculations would become extremely complicated with the chosen method (described in 3.3) .
3. The column or heat exchanger dimensions are not taken into consideration because optimisation of the effects of the design variables on the separation is examined and not on the column itself.
4. Bottom and distillate are boiling liquids.
5. No changes in time occur. So, a stationary operation is assumed.

2.5 Exergy analysis

2.5.1 First law

The conventional way to analyse processes is with the first law of thermodynamics:

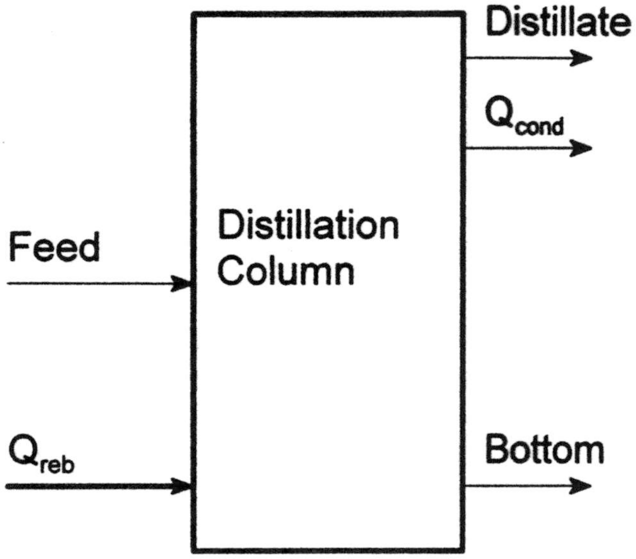

Figure 2.2 : Black box of a distillation column

$$\Delta\left[\left(H+\frac{1}{2}u^2+zg\right)\dot{m}\right]=\dot{Q}-\dot{W}_S \qquad (2.1)$$

In this thesis the kinetic and potential energies are neglected. And if a distillation column is considered as a black box, one mass flow is coming in, the feed, and two are coming out, the distillate and the bottom (see figure 2.2). At the reboiler a heat flow comes in and at the condenser a heat flow comes out. So, the first law is rewritten as:

$$\dot{m}^F H_{liq}^F - \dot{m}^B H_{liq}^B - \dot{m}^D H_{liq}^D + Q_{reb} - Q_{cond} = 0 \qquad (2.2)$$

With this equation a lot of improvements for a distillation can be made clear. If a reduction of the energy demand is achieved by some kind of improvement, this will become obvious. But if this improvement leads to a higher recovery or a lower number of trays, the first law will give almost the same values. So, for these cases the distinguishing power of the first law is very limited. As this thesis will deal a lot with this kind of analyses, the first law is not very useful on its own for these purposes.

2.5.2 Second law

In order to make these improvements visible, the second law of thermodynamics is used:

$$\Delta\dot{S}_{total} \geq 0 \qquad (2.3)$$

This law means that every process proceeds in such a direction that the total entropy change associated with it is positive. The entropy change of heat can be written as the duty divided by the temperature of a reservoir with which the heat exchange takes place. As the entropy change of work is zero, this equation can now be rewritten as:

$$\Delta\dot{S}_{total} = \sum \dot{m}_{out} S_{out} - \sum \dot{m}_{in} S_{in} + \sum \frac{\dot{Q}}{T} \qquad (2.4)$$

A reservoir is a body of constant volume in stable equilibrium in which all energy forms are stored, received and delivered reversibly without a finite change. As the natural environment is the reservoir with which all mass and heat exchanges can be returned, the second law becomes:

$$\Delta\dot{S}_{total} = \Delta\dot{S}_{system} - \frac{\dot{Q}_0}{T_0} \geq 0 \qquad (2.5)$$

For reversible processes the total entropy production is zero and then the entropy production of the system is the same as entropy production due to the heat exchange with the environment. But in reality this is never the case because always entropy is produced due to friction. So, the entropy production is a measure for the degradation of energy during a process. And therefore it is also a measure for the lost opportunities to do work. During the last decades several analysis tools have made use of this entropy production rate. In this thesis the most advanced and fundamental method currently available is chosen: exergy analysis. This analysis method is also known as availability analysis.

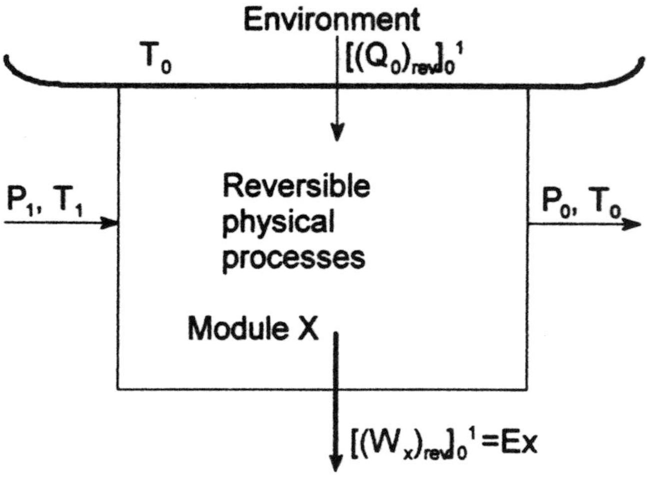

Figure 2.3 : Reversible module

2.5.3 **Definition of exergy**

According to Szargut [22] the definition of exergy is:
Exergy is the maximum amount of work obtainable when some matter is brought to a state of thermodynamic equilibrium with the common components of the natural surroundings by means of reversible processes, involving interaction only with the above mentioned components of nature.

The maximum obtainable work (i.e. exergy) from mass streams, heat, work and mixing will be discussed in the following subchapters.

2.5.4 **Stream of matter**

When a stream of matter is brought back from P_1 and T_1 to the environmental conditions P_0 and T_0, this is done reversibly in an imaginary reversible module, in which the maximum amount of work is obtained from this process. This module is presented in figure 2.3 (Kotas[12]).

The derivation of this amount of work starts with the second law of thermodynamics. For a reversible process the total entropy production is zero and the only exchange with the environment is reversible heat transfer. So equation (2.5) is rewritten as:

$$\left[(Q_0)_{rev}\right]_1^0 = T_0(S_o - S_1) \qquad (2.6)$$

The first law gives for this reversible module:

$$\left[(Q_0)_{rev}\right]_1^0 - \left[(W_s)_{rev}\right]_1^0 = H_o - H_1 \qquad (2.7)$$

Filling equation (2.6) into (2.7) gives the maximum obtainable amount of work and thus also the exergy content of a stream of matter, which is also called the physical exergy:

$$Ex_{phys} = (H_1 - H_0) - T_0(S_1 - S_0) \qquad (2.8)$$

2.5.5 **Heat**

The exergy of heat is in fact derived by Carnot. For the complete derivation is referred to appendix 10.2. If heat is transported in a heat engine from a high temperature T_{high} to a lower temperature T_{low}, the maximum amount of work can be obtained by the Carnot factor:

$$\dot{W}_{rev} = \eta \dot{Q}_{high} \qquad (2.9)$$

Where η is the Carnot factor with which heat can be transferred to work. Carnot derived for this efficiency:

$$\eta = \frac{\dot{W}_{rev}}{\dot{Q}_{High}} = \frac{\dot{Q}_{High} - \dot{Q}_{Low}}{\dot{Q}_{High}} = \frac{T_{High} - T_{Low}}{T_{High}} \qquad (2.10)$$

Translating this to exergy, where heat is transferred from a constant temperature T to the environmental temperature:

$$\dot{Ex} = \dot{Q}\left(1 - \frac{T_0}{T}\right) \tag{2.11}$$

2.5.6 **Work**

The exergy for work is simple:

$$\dot{Ex} = \dot{W}$$

2.5.7 **Mixing**

The exergy of mixing is the maximum obtainable work when the pure components are mixed at environmental conditions P_0 and T_0. So, it is only dependant on the concentrations. The same kind of derivation as for a stream of matter gives an analogue equation:

$$Ex_{mix} = \Delta_{mix}H_0 - T_0\Delta_{mix}S_0 \tag{2.12}$$

So, the exergy of a stream of matter containing a mixture becomes:

$$Ex = Ex_{phys} + Ex_{mix} \tag{2.13}$$

2.5.8 **Chemical exergy**

Chemical exergy of a pure component is the maximum obtainable work at P_0 an T_0 if that component is transformed with the components of the environment into the components of the environment. As in distillation no chemical reactions occur the chemical exergy is not taken into account. So, only the exergy of mass flows, heat, work and mixing are used.

2.5.9 **Exergy loss**

The exergy loss of a process is obtained by the exergy balance where the total exergy input is subtracted from the total exergy output:

$$\dot{Ex}_{loss} = \sum \dot{Q}\left(1 - \frac{T_0}{T}\right) - \sum W_S - \Delta(\dot{m}_j H_j) + T_0\Delta(\dot{m}_j S_j) \tag{2.14}$$

This exergy loss gives the loss of work during the process. And this loss gives much more insight than the application of the first law. If two columns with another design but with the same energy demand and performance are compared, the column with the least exergy loss will be the best design because it uses the available work capacity better. This quality will be shown to be very useful for the types of analyses that will be done in this thesis.

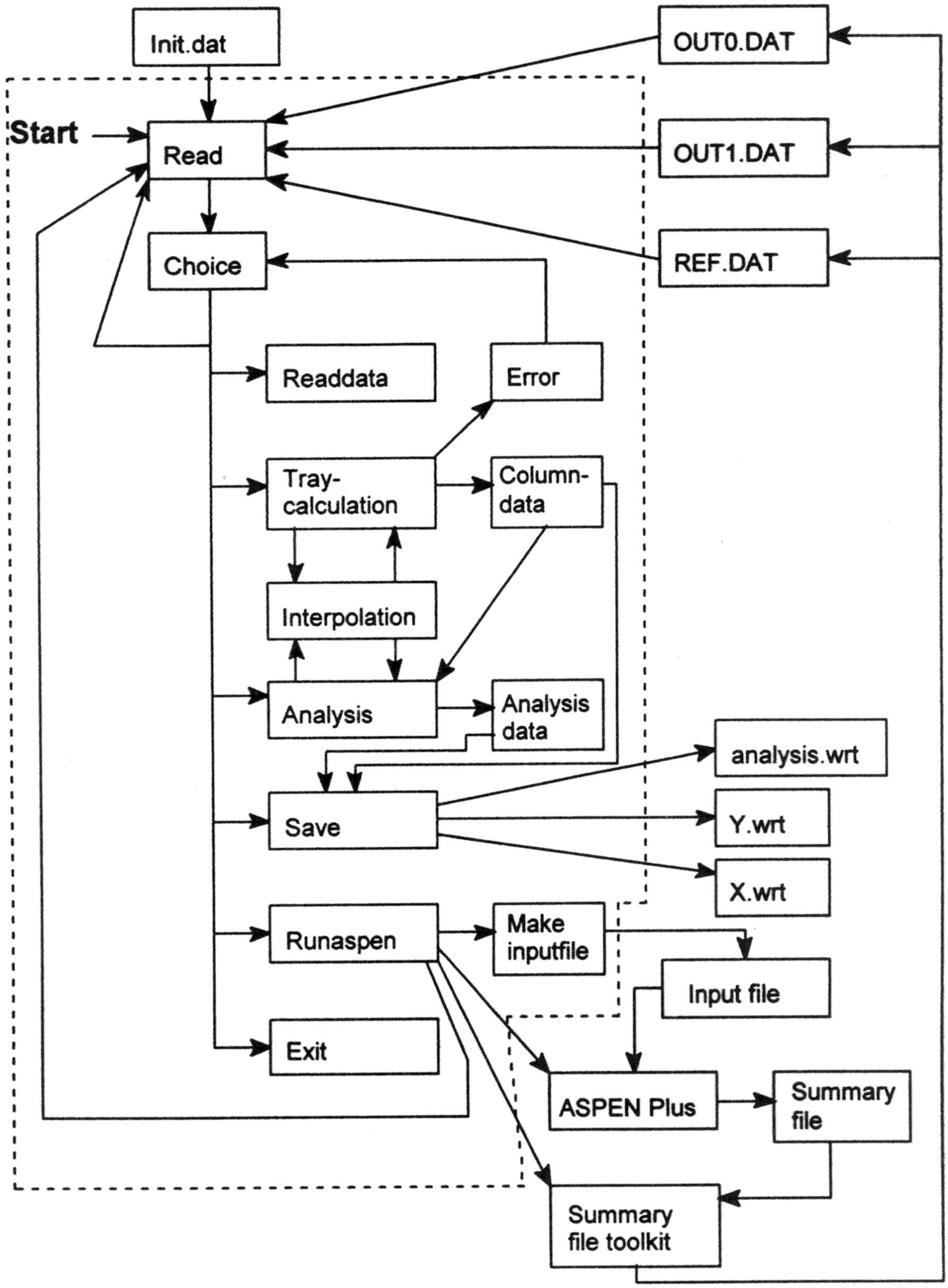

Figure 3.1 : Scheme of the C program

3. Implementation in C

3.1 Introduction

For the calculations for the feed tray analysis and for the location of the interstage heat exchangers the results are generated with a program written in the programming language C. This program is mainly developed at the RWTH Aachen and based on Knoche[11]. The big advantage of an own program is that it is possible to make the assumptions and calculation methods/equations flexible. This was not possible if available software like Aspen Plus was used. This chapter will treat all the important aspects of this program. After a short description of the program, the calculation method will be discussed: the tray-to-tray-calculation. Secondly the new and fast way of calculating the Vapour/Liquid Equilibria(VLE) data will be explained. Afterwards the way of estimating the reflux ratio will be discussed and finally the limitations of the method will be pointed out.

The programming language C is an unstructured one, i.e. it does not work with lines but with functions. This enables an easy creation of a function diagram, which is given in figure 3.1. The part in the box bounded by the dashed line is the program and all the other boxes outside the boundary are external programs or data files. A short explanation of the function diagram is given by commenting the functions:

Read
The program starts with the function read, which reads all the data coming from the init.dat, OUT0.DAT, OUT1.DAT and REF.DAT files. The Init.dat file contains the values of the parameters for the distillation column like the feed flow, pressure, feed mole fractions, recoveries, factor for the reflux ratio etc. (see also appendix 10.8) The other three files contain the Vapour-Liquid Equilibrium data necessary for the interpolation function. All these data are put in the memory and are available throughout the program.

Choice
Here the choice is made by the user what function the program will do. In fact it is the centre of the program.

Readdata
With this function all kinds of equilibrium data can be read and printed on the screen. It was mainly used to check the interpolation during its creation.

Traycalculation
This function performs the simulation of the distillation column. The results are stored in the memory and are called the column data in the scheme. If an error occurs, the function returns automatically to the choice function.

Interpolation

Here the equilibrium calculations are done. The input contains mole fractions. The output consists of the equilibrium mole fractions, enthalpies, entropies and temperatures corresponding to the input mole fractions. Also enthalpies and entropies at environmental conditions can be extracted for the exergy analysis.

Analysis
A total analysis of the column is done with the column data and the interpolation function. The main results are the enthalpy, entropy and exergy balances. This function is also used for the calculation of the fluxes and forces, which are required for the application of the principle of equipartition of forces.

Save
The mole fractions and the analysis data of the trays are saved into external files.

Runaspen
First it reads the data from init.dat again and makes with these data the input file. This file contains the instructions for calculating the VLE-data with the flowsheet program Aspen Plus. This program creates a Summary-file, which contains all the results. The Aspen summary file toolkit is able to read this Summary-file and creates the final VLE data files, which can be read by the function read (see also appendix 10.10). So, this function delivers the data necessary for the interpolation function. This function is only used when new data files for the interpolation function are necessary.

Exit
The program is terminated.

3.2 Tray-to-tray calculations

3.2.1 Introduction

For the calculation of the configuration and settings of the column an old method is chosen: tray-to-tray calculation. This method was the first one with which rigorous calculations were possible. At the moment more modern rigorous methods are available in various programs like Aspen Plus, ChemCad and ChemSep based on simultaneous solving of matrices. The tray-to-tray method has two big advantages above the modern ones. The first one is that for the modern methods the number of trays and the feed tray location must be known before the calculation starts and are therefore not a result of the calculations. And this is a very fundamental difference because a direct feed tray analysis is not possible with the modern methods! The second advantage is that the optimisation criteria that are based on for example exergy can be implemented directly in the calculations. So, only one configuration is calculated and is directly the most optimal one. With the modern methods several column configurations must be analysed before the most optimal one can be determined.

3.2.2 Mole fractions in the distillate and bottom

Before the calculations start, the feed flow, feed mole fractions and the recoveries should be known and these are as previously mentioned obtained from the init.dat file and the function read. The next step is the determination of the mole fractions in the distillate and bottom. Here a few assumptions are made. All the heavy non-keys in the distillate and the light non-keys in the bottom are taken zero. So, the light non-keys are going totally over the top and the heavy non-keys over the bottom. There is always one product flow where the mole fraction of one non-key is zero because in multi component distillation always one non-key component is present.

The mole fractions of the heavy non-keys in the bottom are written as:

$$x_{i,HnK}^{B} = \frac{x_i^F}{\sum_{HK}^{m} x_i^F} \tag{3.1}$$

The sum in the denominator is the sum of the heavy non keys and the mole fraction of the heavy key. The mole fractions of the light non-keys in the distillate are described with:

$$x_{i,LnK}^{D} = \frac{x_i^F}{1-\sum_{HK}^{m} x_i^F} \tag{3.2}$$

For the light key and heavy key in the distillate:

$$\mathrm{x}_{\mathrm{LK}}^{\mathrm{D}} = \mathrm{P}^{\mathrm{D}} * \left(1-\sum_{1}^{\mathrm{LK}-1} \mathrm{x}_{\mathrm{i}}^{\mathrm{D}}\right) \tag{3.3}$$

$$\mathrm{x}_{\mathrm{HK}}^{\mathrm{D}} = (1-\mathrm{P}^{\mathrm{D}}) * \left(1-\sum_{1}^{\mathrm{LK}-1} \mathrm{x}_{\mathrm{i}}^{\mathrm{D}}\right) \tag{3.4}$$

For the light key and heavy key in the bottom:

$$\mathrm{x}_{\mathrm{LK}}^{\mathrm{B}} = (1-\mathrm{P}^{\mathrm{B}}) * \left(1-\sum_{\mathrm{HK}+1}^{\mathrm{m}} \mathrm{x}_{\mathrm{i}}^{\mathrm{B}}\right) \tag{3.5}$$

$$\mathrm{x}_{\mathrm{HK}}^{\mathrm{B}} = \mathrm{P}^{\mathrm{B}} * \left(1-\sum_{\mathrm{HK}+1}^{\mathrm{m}} \mathrm{x}_{\mathrm{i}}^{\mathrm{B}}\right) \tag{3.6}$$

With these mole fractions the decision has to be made at which product flow the calculations are started. The two options are at the distillate or at the bottom. Generally can be said that the calculation starts at the least pure fraction. For two components it is easy: if the feed mole fraction of the light key is larger than the mole fraction of the heavy key the calculations are started at the distillate and if it is smaller at the bottom. With more than two components, one of the mole fractions in either the distillate or at the bottom becomes zero due to the above stated assumptions. The calculation is started at the product flow where none of the mole fractions are zero because otherwise the component with a mole fraction of zero will not be present in the section(stripping or rectifying) where the calculation starts. As this component is present in the feed, the feed balance will not be correct and give negative mole fractions.

3.2.3 **Bottom and distillate flows and the condenser and reboiler duties**

For the start of the tray-to-tray calculations the feed flow, distillate flow and bottom flow together with the mole fractions and the reflux ratio should be known. These are the usual specifications for the calculation of a distillation column and are calculated with the following set of equations:

$$B = F\frac{x_F^{HK} - x_D^{HK}}{x_B^{HK} - x_D^{HK}} \tag{3.7}$$

$$D = F - B \tag{3.8}$$

If the calculations are started at the bottom only the L^1 and the V^1 are required:

$$V^1 = \psi R_{\min} B \tag{3.9}$$

$$L^1 = V^1 - B \tag{3.10}$$

If the calculation starts at the distillate only the L^{N+1} and the V^{N+1} are used:

$$V^{N+1} = (\psi R_{\min} + 1)D \tag{3.11}$$

$$L^{N+1} = V^{N+1} - D \tag{3.12}$$

The two reflux ratios are calculated differently for the two starting points, but this will be explained in chapter 3.5.

For the calculation from the bottom, the duties of the reboiler and condenser can now be calculated with an energy balance over the reboiler and the total column. As the necessary enthalpies are dependent on the mole fractions, these should be known beforehand. As the mole fractions in the bottom flow are known, the y_i^1 in V^1 are obtained from the equilibrium between B and V^1. Usually, an equation of state or/and a model for the activity coefficients is used for this. But here a new and very fast concept is used for the calculation of equilibria data. It consists of a combination of a grid with equilibrium data and an interpolation technique. This method is described in 3.3. Once the y_i^1 in V^1 are known due to the equilibrium, the next step is to calculate the liquid mole fractions x_i^1 in L^1. This is done with the following mass balance over the reboiler:

$$x_i^1 = \frac{V^1 y_i^1 + B x_i^B}{L^1} \tag{3.13}$$

As all the necessary flows and mole fractions are known, the reboiler duty is calculated with an energy balance over the reboiler:

$$Q_{reb} = V^1 H_{vap}^1 + B H_{liq}^B - L^1 H_{liq}^1 \tag{3.14}$$

And the overall energy balance gives the condenser duty:

$$Q_{cond} = Q_{reb} + rFH_{vap}^F + (1-r)FH_{liq}^F - DH_{liq}^D - BH_{liq}^B \tag{3.15}$$

And if the calculations start at the distillate, the mole fractions in L_{N+1} (x_i^{N+1}) are obtained from the equilibrium between D and L_{N+1}. A similar mass balance like (3.13) gives the vapour mole fractions:

$$y_i^{N+1} = \frac{L^{N+1}x_i^{N+1} + Dx_i^D}{V^{N+1}} \qquad (3.16)$$

When the mole fractions are used to obtain the enthalpies of the flows, the energy balance over the condenser gives the condenser duty:

$$Q_{cond} = V^{N+1}H_{vap}^{N+1} + DH_{liq}^D - L^{N+1}H_{liq}^{N+1} \qquad (3.17)$$

Finally, the overall energy balance the reboiler duty:

$$Q_{reb} = DH_{liq}^D + BH_{liq}^B + Q_{cond} - rFH_{vap}^F - (1-r)FH_{liq}^F \qquad (3.18)$$

3.2.4 **Flows and mole fractions in the stripping section**

Only the calculation starting from the bottom will be explained in detail. The calculation from the distillate is exactly the same but than downwards instead of upwards.

For all the equations the tray numbering will be general. The way the trays, flows and mole fractions are numbered is already described in figure 2.1 and is very important for understanding the equations. The basis for the equations on tray n are the known mole fractions and flows of the tray below (n-1). The calculation start at tray no. 2 and the mole fraction and flows of tray no. 1 are known from the reboiler calculations (see equations (3.13), (3.14) and (3.15)).

The first step is to calculate the vapour mole fractions y_i^n on stage n. As the vapour mole fractions y_i^n are in equilibrium with the liquid mole fractions x_i^{n-1} of stage n-1, these are calculated with the interpolation technique. As here the assumption of equimolar overflow is not taken into account, the value of L^n is not the same as L^{n-1}. So, the mass and energy balances must be solved with not enough information. To solve this problem an iteration procedure is used with L^{n-1} and V^{n-1} as initial values. The first iteration loop is started with the first estimation of the liquid mole fractions:

$$x_i^n = \frac{V^{n-1}y_i^n + Bx_i^B}{L^{n-1}} \qquad (3.19)$$

The next step is the calculation of the enthalpies of the liquid and vapour flow with these estimations. These are obtained with the same interpolation procedure that is used for the equilibrium mole fractions. Now the first estimation for the vapour flow is calculated with the energy balance:

$$V^n = \frac{BH_{liq}^B + L^{n-1}H_{liq}^n + Q_{reb}}{H_{vap}^n} \qquad (3.20)$$

And the new value for the liquid flow is obtained with the following mass balance:

$$L^n = V^n + B \qquad (3.21)$$

The last step of one iteration loop is the checking of the energy balance with the new values:

$$\frac{\delta E}{\delta t} = L^n H_{liq}^n + Q_{reb} - H_{vap}^n V^n - BH_{liq}^B \qquad (3.22)$$

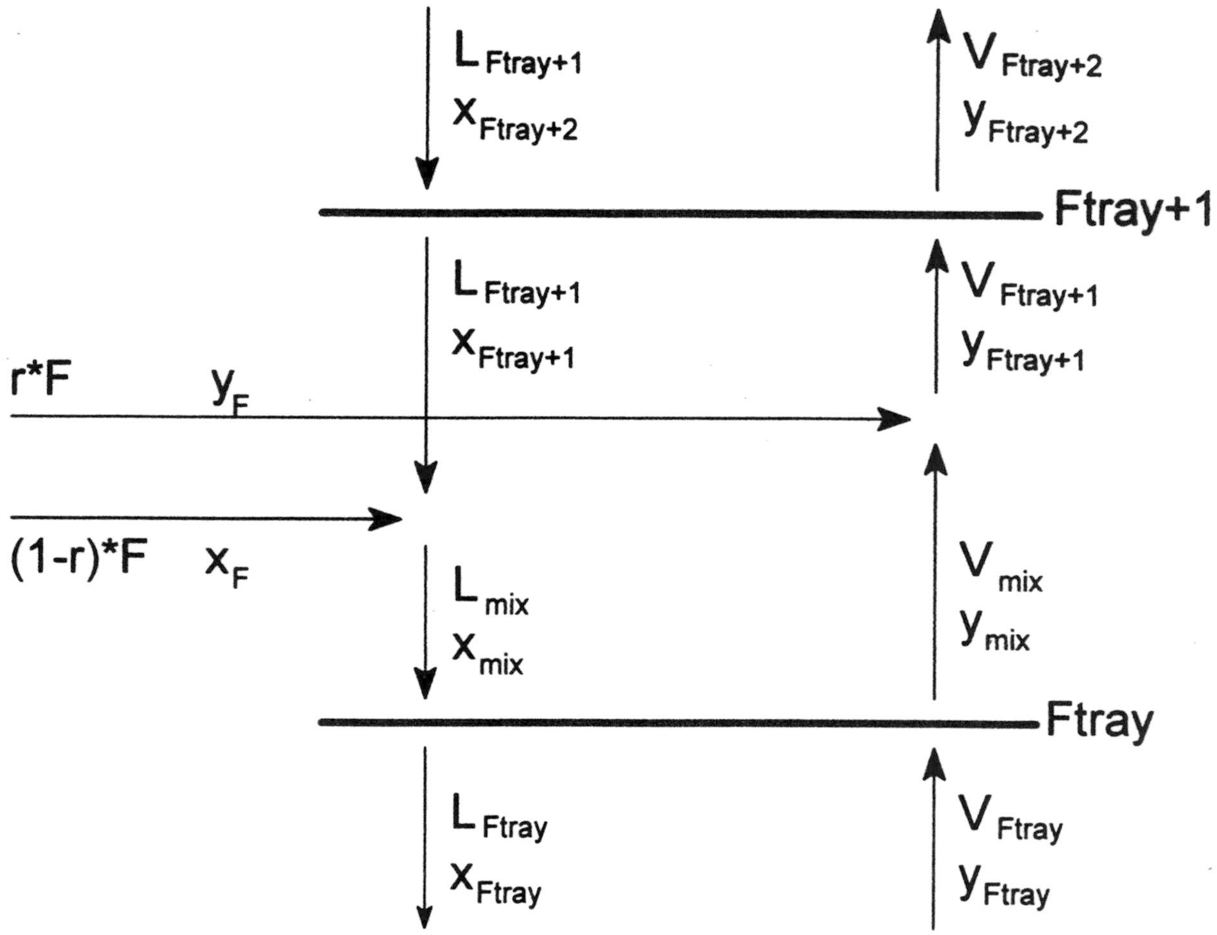

Figure 3.2 : Detail around the feed tray

If this value deviates more than 0.1 Watt from zero the interpolation loop is done another time starting with equation (3.19) and for L^{n-1} and V^{n-1} the recently obtained values of L^n and V^n are used. If the energy balance does not deviate any more than 0.1 Watt, the iteration is stopped and the calculations for the next tray can start with the values of the previous tray with the same balances. These tray-to-tray calculations are done until the number of trays n has reached the value of the feed tray. This feed tray number can be determined with several criteria which minimise the effects of the feed entering. But this will be extensively discussed in chapter 5.

3.2.5 **Mole fractions and flows at the feed**

At the feed four different flows are present under one plate as already could be seen in figure 2.1. A detail of the feed is given in figure 3.2. In order to make a distinction, another subscript 'mix' is given to the flows and mole fractions, which are calculated before the feed is entered. These values are already known because there the stripping calculations have stopped. The flows and mole fractions under Ftray+1 are calculated with the following equations:

$$V^{Ftray+1} = V^{mix} + rF \qquad (3.23)$$

$$L^{Ftray+1} = L^{mix} + (1-r)F \qquad (3.24)$$

$$V^{Ftray+1} y_i^{Ftray+1} = V^{mix} y_i^{mix} + rFy_i^F \qquad (3.25)$$

$$L^{Ftray+1} x_i^{Ftray+1} = L^{mix} x_i^{mix} - (1-r)Fx_i^F \qquad (3.26)$$

In the program the feed concentration is a variable. As the inputs for the feed from the 'init,dat' file are the liquid mole fractions, an equilibrium calculation with the interpolation technique is done to calculate the corresponding vapour mole fractions. Remind that in a process design situation the feed is a given fact and cannot be changed.

The mixing on the feed tray occurs separately from the equilibrium step on the feed tray and therefore the mixing and the equilibrium step can be considered as two separate phenomena. This separation is important for the feed tray analysis in chapter 5. It is also assumed that during the mixing of the two saturated liquids no evaporation takes place and at the mixing of the two saturated vapours no condensation occurs. It is simply not possible to do the calculations for these relatively small phenomena with the available equilibrium calculation method.

3.2.6 **Mole fractions and flows in the rectifying section**

In order to do calculations and iterations for the rectifying section, another set of balances is used in an analogue way as in the stripping section. The first starting point is of course the values of tray number Ftray+1, which are known from the feed tray calculations. These new balances for the iterative procedure are:

$$x_i^n = \frac{V^{n-1} y_i^n - Dx_i^D}{L^{n-1}} \qquad (3.27)$$

$$V^n = \frac{L^{n-1} H_{liq}^n + DH_{liq}^D + Q_{cond}}{H_{vap}^n} \qquad (3.28)$$

$$L^n = V^n - D \qquad (3.29)$$

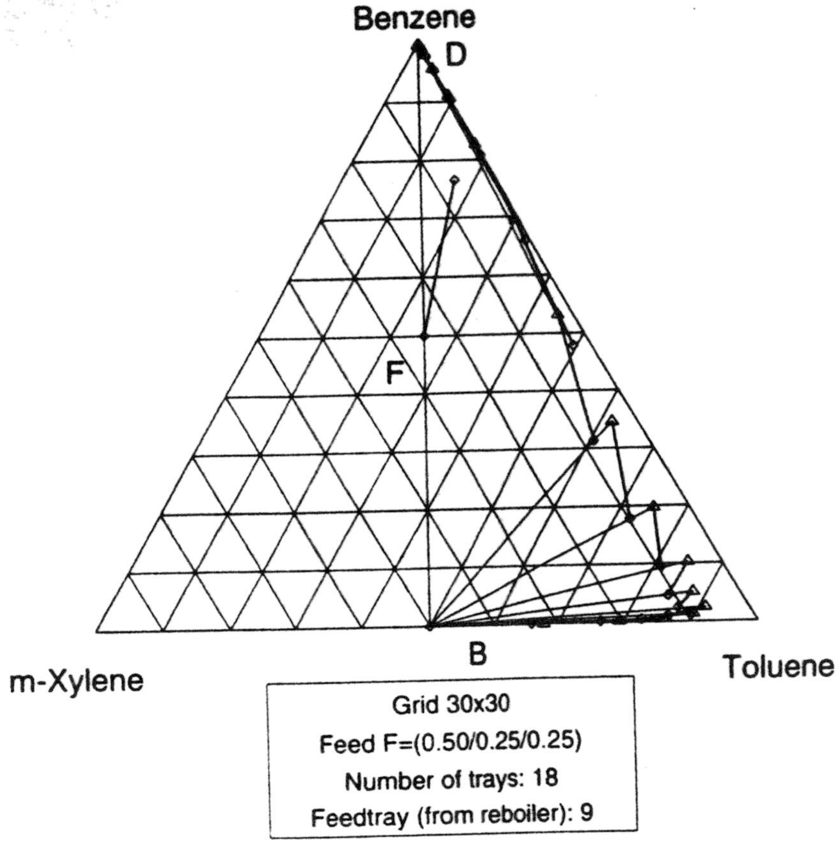

Figure 3.3 : McCabe-Thiele triangle for a simulation started at the bottom

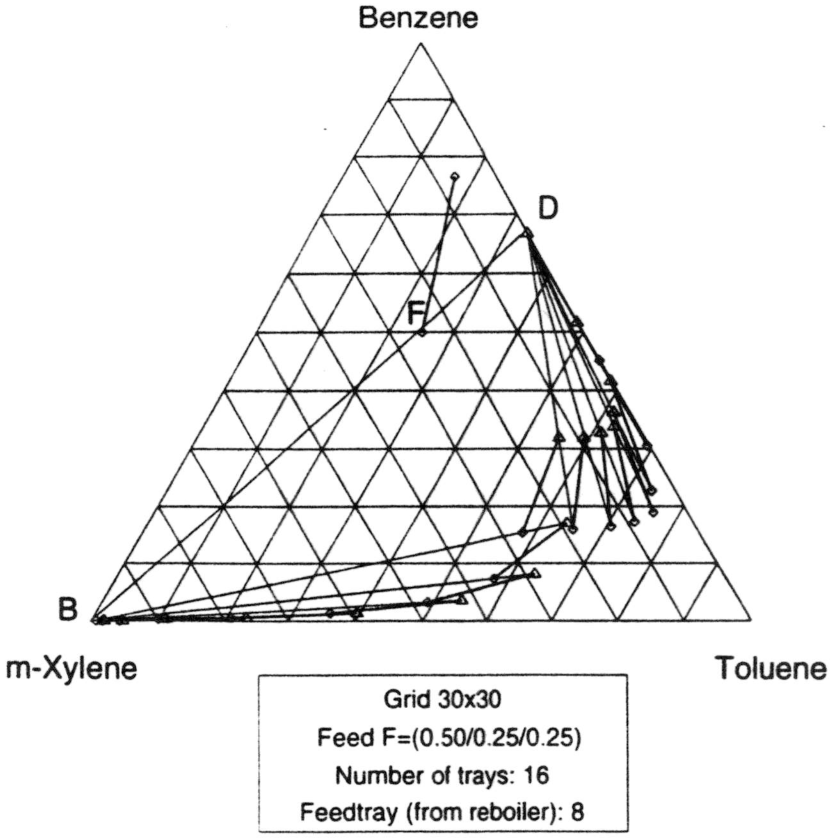

Figure 3.4 : McCabe-Thiele triangle for a simulation started at the distillate

$$\frac{\partial E}{\partial t} = L^n H^n_{liq} + DH^D_{liq} + Q_{cond} - V^n H^n_{vap} \tag{3.30}$$

If the value of the vapour mole fraction of the light key has exceeded the already calculated x_{LK}^D in equation (3.3) the calculations stop and the simulation of the column is ready. The value of n, where the calculation stops, is the total number of trays. It is almost impossible that the value of x^D is the same as the result of equation (3.3) because the calculations are done with discrete equilibrium steps. This fact results in a consequent error in the rectifying section because the incorrect values for x_i^D are used in the balances. Fortunately, this error is very small, e.g. the error in the condenser duty is always less than 0.001 %. The phenomenon that this mole fraction cannot be fixed will be used in the chapter about feed tray analysis.

3.2.7 **Examples**

These calculations result for three component systems in the mole fraction triangles shown in figure 3.3 and figure 3.4.. Figure 3.3 shows the results from a calculation from the bottom where benzene is distilled from toluene and m-xylene. The calculations from the distillate are represented by the points and lines in figure 3.4 where benzene and toluene are distilled from m-xylene. These triangles can be considered as a McCabe-Thiele diagrams for three components. The bold lines represent the equilibria on the trays with the squares as liquid mole fractions(x_i^n) and the triangles as vapour mole fractions(y_i^{n+1}). So, every bold line represents one tray. The thin lines coming from B (=Bottom mole fractions) and D (=Distillate mole fractions) make the connection between the equilibria and represent the working lines resulting from the mass and energy balances. The division between the stripping and rectifying section is given by the origin of these working lines. If the lines come from the D, it is a working line in the rectifying section and if their origin is in B, it is a working line in the stripping section. The ratio between the length of the line starting from B to the square (liquid mole fraction) and the length of the line from B to the triangle (vapour mole fraction) is the internal reflux ratio in the stripping section. In the rectifying section this internal reflux ratio is represented by the length of the total line from D to the square divided by the length of the line between D and the triangle (vapour mole fraction). The bold line at F (= Feed) represents the equilibrium line of the feed.

The specifications of the two columns treated as examples are given in Table 3.1.

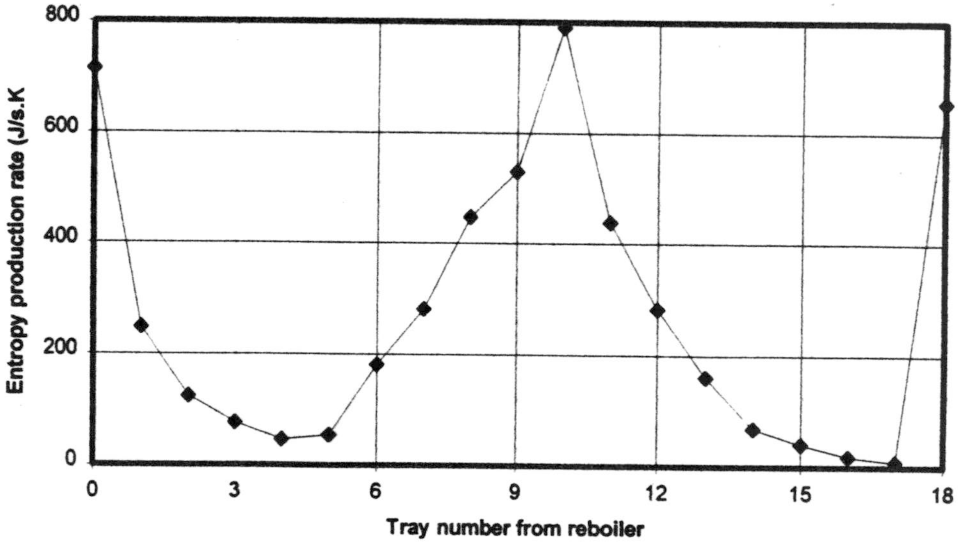

Figure 3.5 : Entropy production rate on each tray

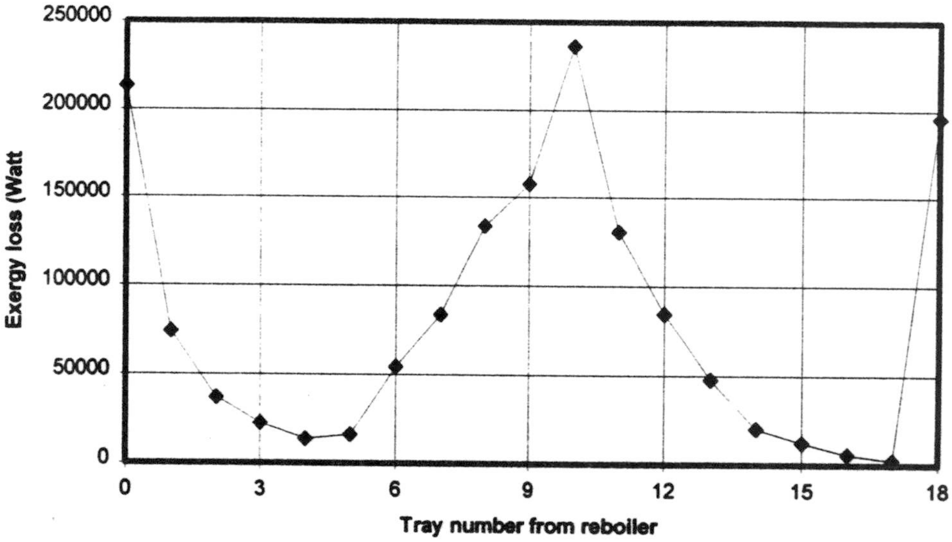

Figure 3.6 : Exergy loss on each tray

Table 3.1: The specifications of the examples in figure 3.3 and 3.4

	Figure 3.3	Figure 3.4
Reflux ratio	9.163	9.927
Number of trays	18	16
Feed tray	9	8
$x^{F}_{Benzene}/x^{F}_{Toluene}/x^{F}_{M\text{-}xylene}$	0.50/0.25/0.25	0.50/0.25/0.25
$x^{D}_{Benzene}/x^{D}_{Toluene}/x^{D}_{M\text{-}xylene}$	0.999/0.001/0	0.66667/0.33300/0.00033
$x^{B}_{Benzene}/x^{B}_{Toluene}/x^{B}_{M\text{-}xylene}$	0.0005/0.4995/0.5000	0/0.0010/0.9990
Feed (mole/s)	100.00	100.00
Bottom (mole/s)	49.95	25.00
Distillate (mole/s)	50.05	75.00
Reboiler Duty (MWatt)	16.12	8.28
Condenser Duty (MWatt)	16.10	8.14

3.2.8 Exergy loss and entropy production rate on the trays

With these results it is also possible to calculate the entropy production rate and the exergy loss on each tray. This is done with the following equations:

$$\Delta\dot{S}_n^{prod} = V_{n+1}S_{n+1}^{vap} + L_n S_n^{liq} - V_n S_n^{vap} - L_{n+1}S_{n+1}^{liq} \qquad (3.31)$$

$$\dot{Ex}_n^{loss} = V_n Ex_n^{vap} + L_{n+1}Ex_{n+1}^{liq} - V_{n+1}Ex_{n+1}^{vap} - L_n Ex_n^{liq} \qquad (3.32)$$

The values for the entropy S are also obtained from the VLE-determination method. Together with the enthalpy H and the enthalpies and entropies at environmental conditions, equation (2.8) and (2.12) give the value for the exergy Ex of the flows.

3.2.9 Exergy loss and entropy production of the reboiler and condenser

The entropy and exergy of the mounts of heat transferred in a heat exchanger like the reboiler and condenser are determined by the temperature in this heat exchanger as can be seen in equation (2.11). This temperature is of course not the same as the boiling temperature of the distillate or bottom. As the condenser removes heat, its temperature should be lower than the boiling temperature of the distillate, i.e. a driving force is necessary. An engineering rule of thumb is that the minimum driving temperature difference for transferring heat is 5° C. So, in order to obtain the temperature in the condenser this driving temperature difference should be subtracted from the boiling temperature of the distillate. The boiling temperatures are again obtained from the interpolation technique. So the equations become for the condenser:

$$\Delta\dot{S}_{cond} = \frac{Q_{cond}}{T_D^{boil} - \Delta T_{driv}} \qquad (3.33)$$

$$\mathrm{E}\dot{\mathrm{x}}_{cond} = \dot{\mathrm{Q}}_{cond}\left(1 - \frac{\mathrm{T}_0}{\left(\mathrm{T}_D^{boil} - \Delta\mathrm{T}_{driv}\right)}\right) \qquad (3.34)$$

As the reboiler adds heat the driving temperature difference should be added to temperature of the bottom:

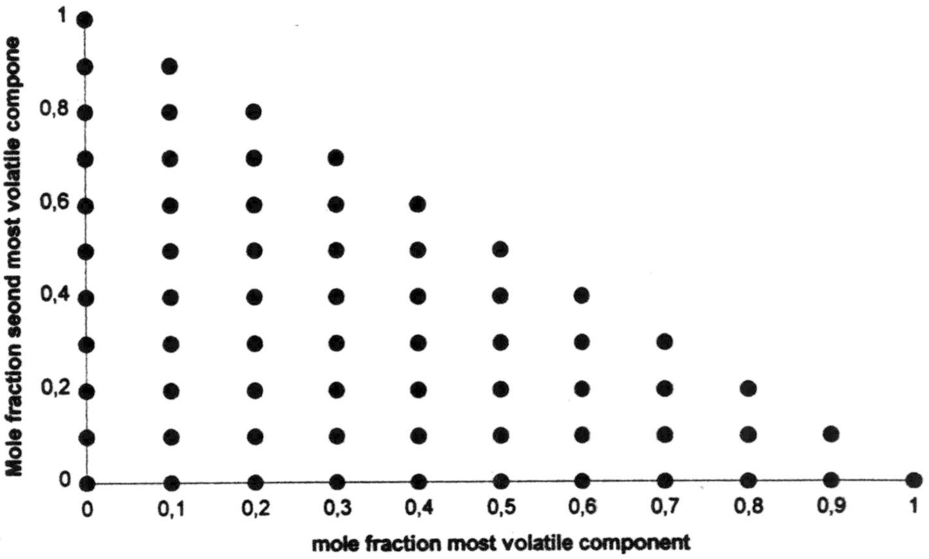

Figure 3.7 : Grid of a three component mixture with gridwidth 0.1

$$\Delta \dot{S}_{reb} = \frac{Q_{reb}}{T_B^{boil} + \Delta T_{driv}} \tag{3.35}$$

$$\mathrm{E\dot{x}}_{reb} = \dot{Q}_{reb}\left(1 - \frac{T_0}{\left(T_B^{boil} + \Delta T_{driv}\right)}\right) \tag{3.36}$$

These contributions to the exergy and entropy are added to the balances in equation (3.31) and (3.32).

For the same example as in figure 3.3 the exergy loss and entropy production rate per tray are calculated. Figures 3.5 and 3.6 show the results. The peaks at the end and beginning of the column are the contributions of the condenser and reboiler. It is quite obvious that around the feed, the reboiler and condenser the largest part of the entropy production and the exergy loss takes place. So, improvements that effect the variables of the feed, reboiler and condenser will probably have the largest effect on the total reduction of entropy production and exergy loss.

3.3 Vapour Liquid Equilibrium Determination

3.3.1 Grid of Vapour Liquid Equilibrium Data

Usually, these equilibrium data are calculated at each stage with an equation of state and/or an equation for activity coefficients. These calculations cost a lot of time, especially for multi component mixtures. To save time, a new concept of determining these values is used: the combination of a grid of VLE data and an interpolation function. First, a file is created with Aspen Plus and the Aspen summary file toolkit, which contains this grid of VLE data. This grid contains not only the values of the liquid mole fractions and the equilibrium vapour mole fractions and vice versa but also the enthalpy values at these liquid or vapour concentrations. For an exergy analysis also the entropies and temperatures are necessary. The main time saving is obtained by doing the time consuming VLE calculations are only once for a certain mixture and pressure.

The first grid is created by variation of the vapour mole fraction of the number of components minus one from 0 to 1 with a certain gridwidth (e.g. 0.1) at a vapour fraction of one (i.e. a condensing vapour). Only the number of components minus one is necessary because the mole fraction of the last component is obtained by the mole balance. The inverse of the gridwidth gives the number of points on the mole fraction axis(for a gridwidth of 0.1 the number of points is 10). Figure 3.7 gives as an example the grid for three components and a gridwidth of 0.1. And at each gridpoint the equilibrium liquid mole fraction, enthalpy, entropy and temperature are calculated with a certain thermodynamic model. So, from this grid the equilibrium liquid mole fractions, enthalpy, entropy and temperature at given vapour mole fractions can be calculated with interpolation.

The second grid is obtained by applying the same method but with the varying of the liquid mole fractions at vapour fraction of zero (i.e., a boiling liquid). So, from this second grid the equilibrium vapour mole fractions, enthalpy, entropy and temperature at given liquid mole fractions can be calculated with interpolation. Finally, the third

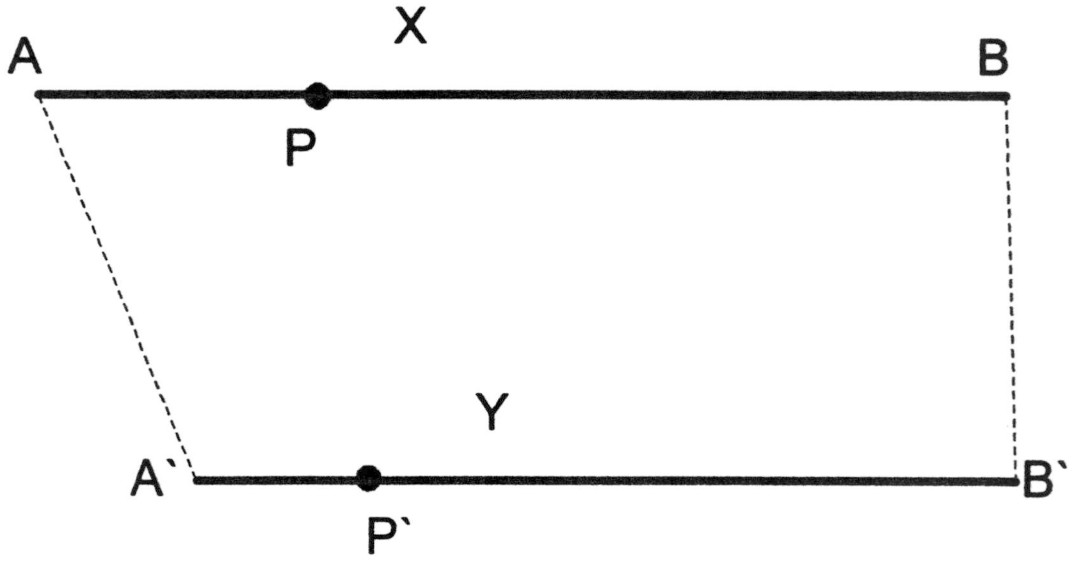

Figure 3.8 : Representation of interpolation in one dimension

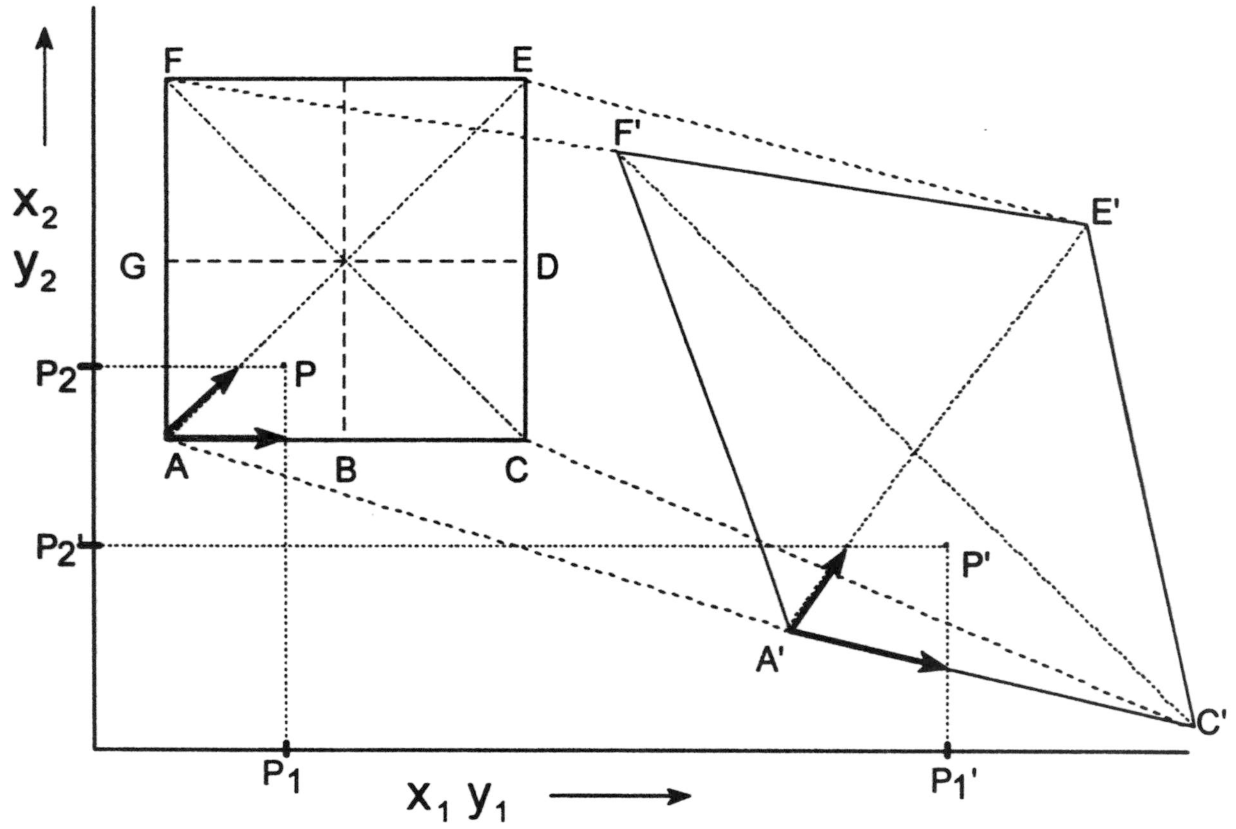

Figure 3.9 : Representation of interpolation in two dimensions

grid is created with varying liquid mole fractions containing the equilibrium enthalpies and entropies at ambient conditions (T 298.15 K, P= 1 bar) for the exergy analysis. So, this implies that all the components used should be in the liquid state at ambient conditions.

These three grids are saved as the OUT0.DAT, OUT1.DAT and REF.DAT files, which are discussed in chapter 3.1.

3.3.2 Thermodynamic Model

The creation of the data necessary for the grids is, as previously mentioned, done with the flowsheet program Aspen Plus. These calculations require a certain thermodynamic model. For this thesis a combination of an activity coefficient model for the liquid phase and an equation of state for the vapour phase is chosen. The most accurate combination supplied by Aspen Plus is the UNIQUAC activity coefficient model and the Redlich-Kwong equation of state. This combination gives small errors because regressed experimental data in the form of binary interaction parameters are used and it enables also calculations for a large variety of mixtures in a large range of temperatures and pressures.

3.3.3 Interpolation technique

The interpolation for two components is relatively easy. This interpolation is illustrated by figure 3.8. As only one component is varied in the grid, the interpolation is one-dimensional. If the vapour mole fractions(P') are asked for liquid mole fractions(P) which are not gridpoints, the first step is to find the enclosing liquid gridpoints A and B in the grid. If these gridpoints are found, the grid gives the vapour gridpoints A' and B' automatically. The actual interpolation is then described by the following equation:

$$P' = A' + \frac{|AP|}{|AB|}|A'B'| \tag{3.37}$$

For three and more components it is more complicated. The interpolation takes place in two dimensions for three components and for four components in three dimensions etc. In two dimensions one point is enclosed by four points and in three dimensions by eight etc. (see figure 3.9). This number of gridpoints is available for interpolation. For interpolation in more than one dimension one point is already fixed: the base point from which the interpolations into all the dimensions takes place. This base point is of course the closest gridpoint to the point on which the interpolation is performed. For a correct interpolation also a number of construction gridpoints is necessary. As this number is equal to the number of dimensions, there are more gridpoints available than necessary and a choice has to be made. This choice will be explained for three components, but is completely analogous to four and more components.

As an example, the interpolation will be explained that obtains the equilibrium vapour mole fractions at given liquid mole fractions. The basis for this is figure 3.9. The x-axis represents the liquid mole fraction or vapour mole fraction of the most volatile component and the y-axis of the second most volatile component. The mole fraction of the third (and least volatile) component can easily be calculated as the sum of the

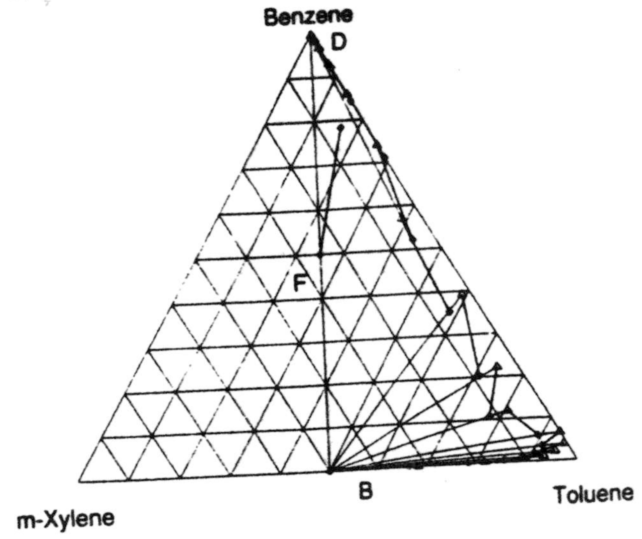

Figure 3.10 : McCabe-Thiele triangle for a 10x10 grid (gridwidth 0.1)

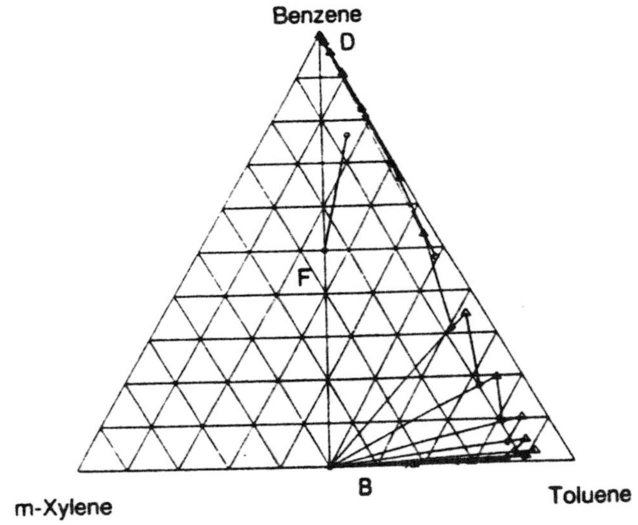

Figure 3.11 : McCabe-Thiele triangle for a 30x30 grid (gridwidth 0.0333)

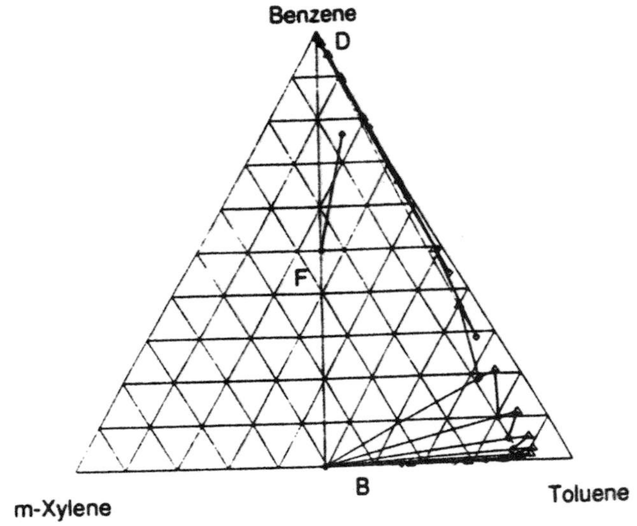

Figure 3.12 : McCabe-Thiele triangle of the Aspen Plus results

fractions must be one. And all the points in the figure have two values: one for the first component and one for the second component. The angular points of the square represent the gridpoints of the liquid mole fractions available for the interpolation and of the quadrangular the vapour mole fractions that are in equilibrium with the gridpoints. Clearly the square is transformed. Note that the lengths of the edges of the square represent the gridwidth.

If the vapour fractions are asked for the liquid mole fractions represented by point P in the square, the first step is the determination of the closest gridpoint. This is done based on the distance $|A_1P_1|$ and $|A_2P_2|$. If the $|A_1P_1|$ and $|A_2P_2|$ are smaller than $|A_1B_1|$ and $|A_2G_2|$ than A is the closest gridpoint. But if for example $|A_1P_1|$ would be larger than $|A_1B_1|$ the closest point will be C. For a correct interpolation, two more gridpoints are necessary, one to determine the transformation in the x_1-direction and the second for the transformation in the x_2-direction. These transformations can be expressed by two vectors starting from the closest point A. For these vectors are the two straight vectors enclosing the point and the diagonal available. The diagonal is included because it reduces the (inevitable) error. So, for point P the enclosing vectors are $|A_1C_1|$ and $|A_2E_2|$. Now the distances $|A_1P_1|$ and $|A_2P_2|$ are used again. These distances are normalised with the vector distances. These relative distances are multiplied with the distances of the corresponding vectors in the transformation ($|A_1'C_1'|$ and $|A_2'E_2'|$) and the multiplications are summed with vapour mole fractions of point A'. This sum gives the vapour mole fractions. So, written in equations the vapour mole fractions P_1' and P_1' become:

$$P_1' = A_1' + \frac{|A_1P_1|}{|A_1C_1|}|A_1'C_1'| \qquad (3.38)$$

$$P_2' = A_2' + \frac{|A_2P_2|}{|A_2E_2|}|A_2'E_2'| \qquad (3.39)$$

Similar kind of pictures and discussions can be used for the liquid mole fractions, enthalpy, entropy and temperature.

3.4 Accuracy

The accuracy is mainly determined by the amount of gridpoints. If more gridpoints are available the gridwidth decreases. As the distance between the gridpoints decreases with the gridwidth, a more reliable value for the results is obtained. The question is now what is the maximum gridwidth for realistic calculations. As a benchmark for realistic results the calculation method of the radfrac distillation column in Aspen Plus is taken. This radfrac distillation column is the name of one of the rigorous calculation methods for distillation columns available in Aspen Plus. Figure 3.10 shows the results of the simulation of a column with a grid of 10x10 points, i.e., a gridwidth of 0.1. The notation 10x10 refers to the multiplication of the numbers of points on the mole fraction axes. Figure 3.11 gives the results of the same column but with a grid of 30x30 points, , i.e., a grid width of 0.0333. Finally, the benchmark results are represented in figure 3.12. A quick look already shows that the grid with 10x10 gridpoints does not resemble the benchmark results. However the results of the 30x30 grid do not completely coincide with the Aspen results, the resemblance is good enough to conclude that the 30x30 grid gives realistic results. So, For all the simulations in this final thesis a grid of 30x30 will be used.

3.5 Reflux ratio

The reflux ratio is normally defined as the flow returned to the column at the condenser or reboiler divided by the corresponding product flow (see figure 2.1) depending on at which product flow the calculation starts. If the calculations start at the distillate:

$$R = \frac{L^{N+1}}{D} \qquad (3.40)$$

If the calculations start at the bottom:

$$R = \frac{V^1}{B} \qquad (3.41)$$

The best estimate for the minimum reflux ratio for multi component distillation is obtained from the Underwood equations [3].

$$\sum_{1}^{m} \frac{\alpha_i x_i^F}{\alpha_i - \Theta} = 1 - q \qquad (3.42)$$

If the calculations start at the distillate:

$$R_{\min} + 1 = \sum_{1}^{m} \frac{\alpha_i x_i^D}{\alpha_i - \Theta} \qquad (3.43)$$

If the calculations start at the bottom:

$$R_{\min} = -\sum_{1}^{m} \frac{\alpha_i x_i^B}{\alpha_i - \Theta} \qquad (3.44)$$

Where q is defined as:

$$q = \frac{\textit{heat to vaporise 1 mole feed}}{\textit{molar latent heat of feed}} \qquad (3.45)$$

If an ideal gas and an ideal dilution are assumed q is the same as 1-r, i.e. the percentage liquid of the feed.

The first step is the calculation of the constant Θ from equation (3.42). As this equation is not analytically solvable an iterative calculation is necessary. If the Θ is obtained, it is filled into equation (3.43) with the minimum reflux ratio as a result. An example is given in appendix 10.1.

The relative volatilities are the average relative volatilities over the column:

$$\alpha_{av} = \sqrt{\alpha_{top}\alpha_{bottom}} \qquad (3.46)$$

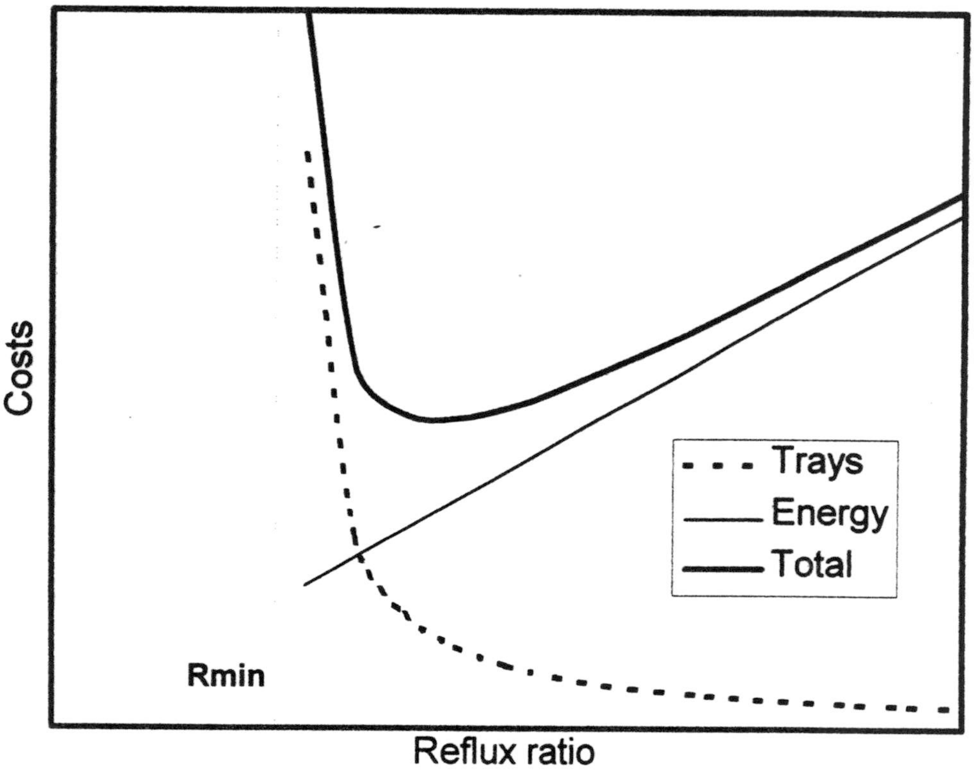

Figure 3.13 : Tray, energy and total costs as a function of the reflux ratio

For the Underwood method all the relative volatilities are taken relative to one component, for example the light key. So, the equation for the relative volatility for all components is given by:

$$\alpha_{i,LK}^{top} = \frac{y_i^D / x_i^D}{y_{LK}^D / x_{LK}^D} \tag{3.47}$$

$$\alpha_{i,LK}^{bottom} = \frac{y_i^B / x_i^B}{y_{LK}^B / x_{LK}^B} \tag{3.48}$$

As for all the columns the distillate and bottom are a saturated liquid, the corresponding equilibrium y-values in equation (3.47) and (3.48) are obtained by the interpolation technique.

At the minimum reflux ratio, the number of trays would be infinite and so a multiplication factor is necessary in order to give a realistic reflux ratio. The multiplication factor is primarily an economical variable and not an engineering variable. The reflux ratio effects the energy duty and the number of trays. With increasing reflux ratio the energy duty increases linearly but the number of trays decreases hyperbolically to a minimum value. The energy duty and the number of trays can be related directly to money costs and the sum of those costs shows an optimum (see figure 3.13). So, in order to make consistent engineering comparisons, the reflux ratio should be taken constant and above the minimum reflux ratio.

The internal reflux ratio, which is already mentioned in the terminology, is described by the following equation:

$$R_n^{internal} = \frac{L_n}{V_n} \tag{3.49}$$

3.6 Limitations

Unfortunately several limitations are found. The first limitation is the internal memory limitation in Aspen Plus. The minimum lattice width with four components is 0.1 (grid 10x10x10) and is therefore not good enough like the comparison of figure 3.9 and 3.10 with 3.11 proved for three components. This problem becomes very obvious at the iteration for the correction for the energy balance. Only a few combinations of feed concentrations and reflux ratios gave logic results. The rest of the results gave too large deviations in the vapour and liquid flows due to convergence problems in the energy balance iteration for the trays.

The second limitation is the separation in the middle (ABCD→AB + CD) of mixtures with four components. This separation is not possible because no suitable assumptions can be made for the mole fractions of the light non-key components in the bottom flow if the calculation is done from the bottom. This is also the case with the mole fractions for the distillate flow of the heavy non-key components if the calculation is done from the distillate. Actually these two limitations imply that the maximum number of components is three for these rigorous calculations with this program.

The last limitation is the accuracy of the mole fractions. The iteration function gives only 5 significant numbers for the mole fractions. So everything less than 0.00001 is taken zero.

3.7 Conclusions

The main conclusion from this chapter is that a good tool is provided for the calculations of the feed tray and interstage heat exchangers in the next chapters. The interpolation technique has proved to give realistic values and the simulations of the columns are also good enough to proceed and base further conclusion on them. The only disappointment is that the limitations of the program only allow the use of three components. For more components other calculation methods or other ways of creating the grids are necessary.

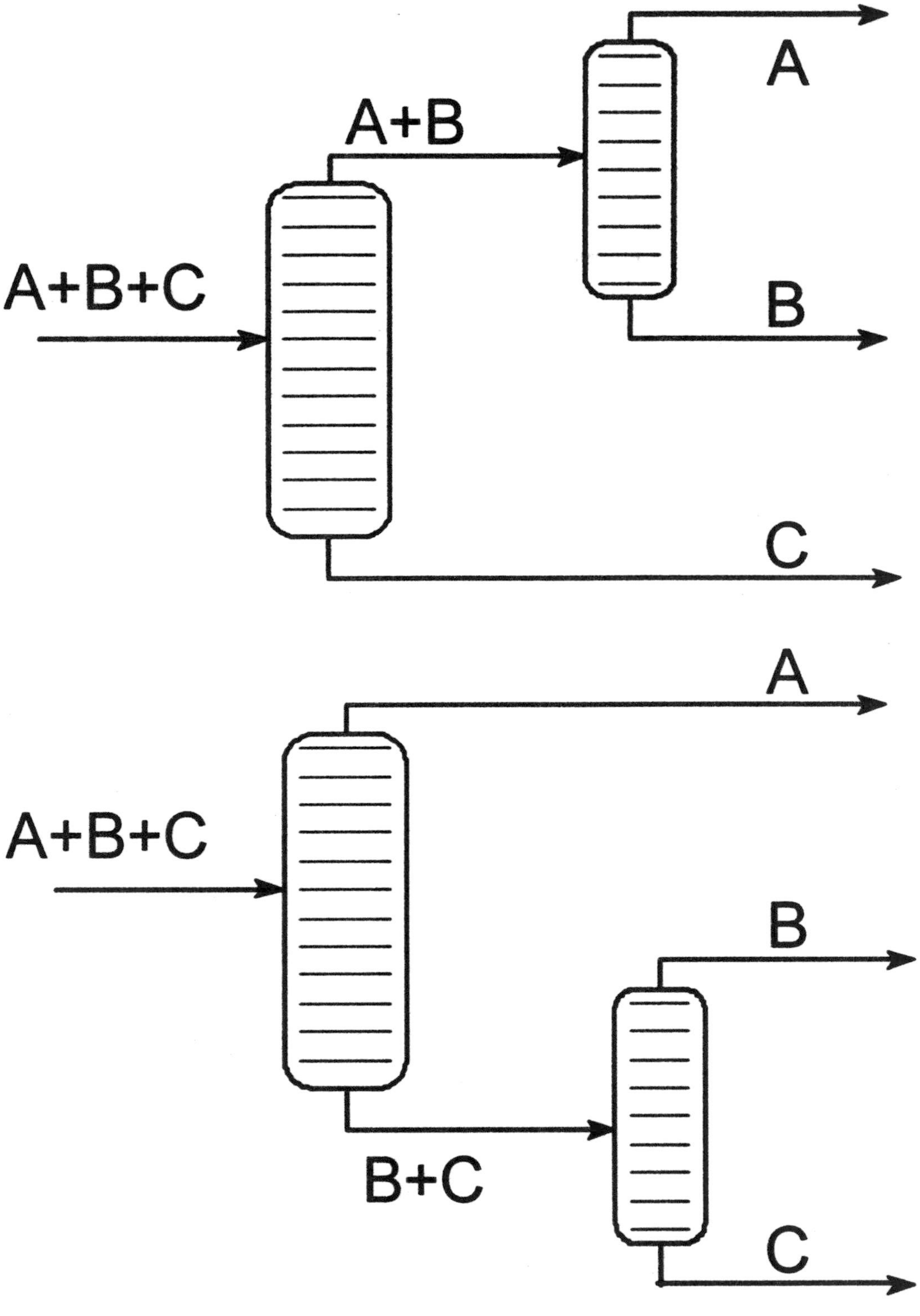

Figure 4.1 : Two different sequences

4. Sequencing

4.1 Introduction

In this chapter the sequencing of distillation columns of a multi component mixture is analysed. If a mixture has to be separated into its pure components, various different sequences of distillation columns are possible depending on the number of components. For example, if a three component mixture(A+B+C) is to be separated into its pure fractions, two columns are necessary, which can be sequenced in two different manners. This is illustrated by figure 4.1. The difference between the sequences is which column performs which separation. If the separation of the lightest component(A) from the heaviest two components(B+C) is done in the first column, the bottom flow will go into the second column and separate the heaviest component(C) from the middle component(B). But if the first column separates the heaviest component(C) from the lightest two components(A+B), the distillate flow will go into the second column to separate the lightest component(A) and the middle component(B). But only one of those two possibilities is the best and this chapter analyses a relatively new approach to this problem: the sum of a performance determining variable of all columns in one sequence. This criterion will be compared with the ultimate criterion, the total annual cost of the sequence. The variables that will be analysed are the vapour load, the ideal exergy loss and the non-ideal exergy loss. This comparison will be done for mixtures with five components.

4.2 Approaches

4.2.1 Heuristics

During the last decades several approaches are developed to point the best sequence. The first and oldest approach is the application of a set of heuristics. A lot of different listings of these heuristics can be found in the literature [9, 13 and 15]. King[9] gives the four most important:

1. Separations where the relative volatility of the key components is close to unity should be performed in the absence of non-key components.
2. Sequences which remove the components one by one in column overheads should be favoured.
3. Sequences which give a more nearly equimolar division of the feed between distillate and bottoms product should be favoured.
4. Separations involving high specified recovery fractions should be reserved until late in the sequence.

The big disadvantage is that some heuristics can be contradictory. For example if a separation has high specified recovery fractions but it leads to an equimolar division of the distillate and bottom, the third heuristic says that it should be favoured and the fourth heuristic says that it should be postponed until the end of the sequence. So, the heuristics do not give a good answer to those problems.

4.2.2 Total simulation

The second approach is a total simulation with a flowsheet program as Aspen plus. The disadvantage is not the calculation time of the computer anymore but the expensive time and effort that an engineer spends to define the flowsheet properly. Flowers[5] is an example of such a rigorous calculation. In this article all the possible sequences of various kinds of mixtures are simulated in Aspen Plus and all the costs are calculated. Clearly this analysis has costed much time but the advantage is that it is the most reliable method available at the moment.

4.2.3 Sum of a variable

The third way is introduced by Porter&Momoh [15] in 1991 and will be analysed further in this chapter. The basis is the calculation of a variable of a single distillation column related with its performance. For each sequence the values of this variable are summed. And the sequence that has the minimum value for this sum should be the best. Porter&Momoh [15] proved that the vapour load was able to do this. Their analysis is repeated and two other variables related to exergy are also tested. In the end these three variables will be compared. The following list gives a short description of the variables with their typical assumptions:

1. Vapour load with equal enthalpies of vaporisation and a simple estimation for the reflux ratio.
2. Exergy loss with equal enthalpies of vaporisation and a simple estimation for the reflux ratio. This criterion will be indicated as ideal exergy loss.
3. Exergy loss with different enthalpies of vaporisation and reflux ratio is determined with the Underwood equations. This criterion will be indicated as non-ideal exergy loss.

It is expected that the exergy losses will be better than the vapour load because they have a better fundamental basis. And it can also be expected that the non-ideal exergy loss will perform better than the ideal exergy loss because two important simplifications are removed.

4.3 Definition & Equations

4.3.1 Assumptions

For the derivation of the ideal exergy loss, non-ideal exergy loss and vapour load in a sequence of distillation columns, the following assumptions are made beside the already stated assumptions in chapter 2.4:

- Sharp separations.
- The ratio between the actual reflux ratio and minimum reflux ratio (symbolised by Ψ) is 1.1.
- Simple columns, no inter-heat-exchangers, no side streams.
- No corrosive components.
- No azeotropes.

4.3.2 Ideal exergy loss

The first variable for assessing the sequences, which will be derived is the ideal exergy loss. In general the exergy loss is described as:

$$\dot{Ex}_{loss} = \sum \dot{Q}(1-\frac{T_0}{T}) - \sum \dot{W}_S - \Delta(\dot{m}_j H_j) + T_0 \Delta(\dot{m}_j S_j) \qquad (4.1)$$

For one distillation column can be written:

$$\dot{Ex}_{loss} = \dot{m}_F(H_F - T_0 S_F) - \dot{m}_B(H_B - T_0 S_B) - \dot{m}_D(H_D - T_0 S_D) + \\ + \dot{Q}_{reb}(1-\frac{T_0}{T}) - \dot{Q}_{cond}(1-\frac{T_0}{T}) \qquad (4.2)$$

As the feed and the products are the same for all the different sequences, these flows can be left out. So, the exergy loss for one sequence becomes:

$$\dot{Ex}_{loss}^{sequence} = \sum_1^j \left[\dot{Q}_{reb}\left(1-\frac{T_0}{T_{reb}}\right) - \dot{Q}_{cond}\left(1-\frac{T_0}{T_{cond}}\right)\right] \qquad (4.3)$$

The heats of vaporisation are assumed to be equal for all components and this means for the ideal exergy loss : $Q_{reb}=Q_{cond}$. The lost exergy is now described by:

$$\dot{Ex}_{loss}^{sequence} = \sum_1^j \left[\dot{Q}T_0\left(\frac{1}{T_{cond}} - \frac{1}{T_{reb}}\right)\right] \qquad (4.4)$$

The heat production in the condenser:

$$\dot{Q}_{cond} = \Delta_{vap}HV = \Delta_{vap}H(\psi R_{min} + 1)D \qquad (4.5)$$

From Clausius -Clapeyron can be derived:

$$\ln(\alpha) = \frac{\Delta_{vap}H}{R^{gas}}\left(\frac{1}{T_{cond}} - \frac{1}{T_{reb}}\right) \qquad (4.6)$$

For a saturated liquid feed the following approximation for the reflux ratio can be made:

$$R_{min} = \frac{F}{(\alpha-1)D} \qquad (4.7)$$

Where α is the relative volatility for ideal mixtures:

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} = \frac{P_1^{sat}}{P_2^{sat}} \qquad (4.8)$$

Taking the lost exergy per one mole initial feed that goes into the first column of the sequence, gives for the feed and distillate:

$$F = x_1^{F,init} + \ldots + x_m^{F,init} \qquad (4.9)$$

$$D = x_1^{F,init} + \ldots + x_{LK}^{F,init} \qquad (4.10)$$

Filling equation (4.5), (4.6), (4.7), (4.9) and (4.10) into (4.4) and

$$\dot{Ex}_{loss}^{sequence} = \sum_{1}^{j}\left[R^{gas}T_0 \ln\alpha\left(\frac{\psi\left(x_1^{F,init}+\ldots+x_m^{F,init}\right)}{1-\alpha}\right)+\left(x_1^{F,init}+\ldots+x_{LK}^{F,init}\right)\right] \tag{4.11}$$

In terms of summations this equation is rewritten as:

$$\dot{Ex}_{loss}^{sequence} = \sum_{1}^{j}\left[R^{gas}T_0 \ln\alpha\left(\frac{\psi\sum_{1}^{m} x_i^{F,init}}{1-\alpha}\right)+\sum_{1}^{LK} x_i^{F,init}\right] \tag{4.12}$$

It is very important for the understanding of this equation that the mole fractions are the mole fractions of the feed which enters the first column, which is called the initial feed. So, only for the first column is $x_1^{F,init} + \ldots + x_m^{F,init} = 1$ valid. But as important as the previous statement is that the first component of a column is not necessarily the first component of the feed which enters the first column but the lightest component which enters this column. For example, if a column performs the separation BC+D in a sequence where component A, B, C, D and E are separated into the pure fractions, the first component is not A but B. Remember that A is not present in that column because sharp separations are assumed. This reasoning is also valid for the last component m. It is the heaviest component coming in the corresponding column.

4.3.3 **Non-ideal exergy loss**

If the heats of vaporisation are not assumed to be equal the non-ideal exergy loss is derived from the same basic equations:

$$\dot{Ex}_{loss}^{sequence} =$$

$$\sum_{1}^{j}\left[\sum_{1}^{LK} x_i^{F,init}\left(\psi\left(R_{min}+1\right)\Delta_{vap}\overline{H}_{reb}\left(1-\frac{T_0}{T_{reb}}\right)-\left(\psi R_{min}+1\right)\Delta_{vap}\overline{H}_{cond}\left(1-\frac{T_0}{T_{cond}}\right)\right)\right] \tag{4.13}$$

This equation is more accurate than equation (4.11) but also needs more information. This extra information consists of the enthalpies of vaporisation and the temperatures in the reboiler and condenser. For the enthalpies of vaporisation and temperatures in the reboiler and condenser the mole fraction average values are taken. So, the enthalpy of vaporisation and temperatures in the condenser are given by:

$$\Delta_{vap}\overline{H}_{cond} = \frac{\sum_{1}^{LK} x_i^{F,init}\Delta_{vap}H_i}{\sum_{1}^{LK} x_i^{F,init}} \tag{4.14}$$

$$T_{cond} = \frac{\sum_{1}^{LK} x_i^{F,init}T_i^{boil}}{\sum_{1}^{LK} x_i^{F,init}} \tag{4.15}$$

And the enthalpy of vaporisation and temperatures in the reboiler are given by:

$$\Delta_{vap}\overline{H}_{reb} = \frac{\sum_{HK}^{m} x_i^{F,init} \Delta_{vap} H_i}{\sum_{HK}^{m} x_i^{F,init}} \tag{4.16}$$

$$T_{reb} = \frac{\sum_{HK}^{m} x_i^{F,init} T_i^{boil}}{\sum_{HK}^{m} x_i^{F,init}} \tag{4.17}$$

The denominators are necessary because of the already mentioned use of the mole fractions.

4.3.4 Vapour load

The third assessment variable is the vapour load. Its derivation is quite similar to the derivation of the exergy loss. The vapour load is given by:

$$V_j = (1 + \psi R_{\min}) D \tag{4.18}$$

The minimum reflux ratio can also be described as(see also equation (4.7)):

$$\mathrm{R}_{\min} = \frac{\mathrm{x}_{\mathrm{D,LK}}}{\mathrm{x}_{\mathrm{F,LK}}(\alpha_{\mathrm{LH}} - 1)} \tag{4.19}$$

The vapour load becomes now:

$$\mathrm{V}_{\mathrm{j}} = \mathrm{D}\left\{\frac{(\alpha_{\mathrm{LH}} - 1) + \psi \frac{\mathrm{x}_{\mathrm{D,LK}}}{\mathrm{x}_{\mathrm{F,LK}}}}{(\alpha_{\mathrm{LH}} - 1)}\right\} \tag{4.20}$$

If the distillate is taken per mole feed:

$$D = x_1 + x_2 + \ldots + x_{LK} = \sum_{1}^{LK} x_i \tag{4.21}$$

The feed and distillate mole fractions of the light key are given by:

$$x_{F,LK} = \frac{x_{LK}}{x_1 + x_2 + \ldots + x_m} \tag{4.22}$$

$$x_{D,LK} = \frac{x_{LK}}{x_1 + x_2 + \ldots + x_{LK}} \tag{4.23}$$

Combining all these equations, the vapour load becomes finally:

$$V = (x_1 + \ldots + x_{LK}) + \frac{\psi}{\alpha - 1}(x_1 + \ldots + x_m) \tag{4.24}$$

So, the equation for the total vapour load of a sequence is, rewritten with respect to the mole fractions:

$$V^{\text{sequence}} = \sum_{1}^{j}\left[\sum_{1}^{LK} x_i^{F,init} + \frac{\psi}{\alpha - 1}\sum_{1}^{m} x_i^{F,init}\right] \qquad (4.25)$$

It is striking that the only significant difference between the exergy loss and the vapour load is the ln(α). Again it is important to realise the correct use of the mole fractions as described in chapter 4.3.2 about the ideal exergy loss.

4.3.5 **Comparison of the criteria**

As a sequencing criterion a variable of a distillation column is used. If the sum of that variable of each column in the sequence is taken, the minimum (or maximum) value of the sums of all sequences determines the best sequence. The question is now: how can the performance of a criterion be tested? The ultimate criterion is of course the Total Annual Cost (TAC), because in the end only the most competitive (= cheapest) sequence is the best. In the literature many cost calculation methods can be found varying from very simple to very rigorous. In order to distinguish properly between the criteria a rigorous method is necessary because the simple methods are in most cases only the multiplication of a technical variable with an empirical proportionality constant. As the criteria used here are technical variables, these simple methods are useless. One of the most rigorous methods is used in Flowers [5] for all 14 sequences of three different mixtures with five components. So, as a benchmark for the comparisons of criteria these TAC's will be used.

4.4 **The mixtures and the sequences**

4.4.1 **The mixtures**

The mixtures and their mole fractions with which the calculations are done are given in Table 4.1.

Table 4.1: The mixtures and their mole fractions

	Mixture 1		Mixture 2		Mixture 3	
	Component	Fraction	Component	Fraction	Component	Fraction
A	n-pentane	0.25	Propane	0.05	Ethanol	0.25
B	n-hexane	0.15	i-butane	0.15	i-propanol	0.15
C	n-heptane	0.35	n-butane	0.25	n-propanol	0.35
D	n-octane	0.10	i-pentane	0.20	i-butanol	0.10
E	n-decane	0.15	n-pentane	0.35	n-butanol	0.15

These mixtures are chosen primarily because for these mixtures Flowers [5] has calculated the Total Annual Costs for all the sequences. But these three mixtures have each an own character. The first mixture is highly ideal with easy separations. The second mixture is also ideal but has some difficult separations. And the third is not very ideal and has difficult separations. So, the criteria will be tested on three different types of mixtures. Porter and Momoh [15] only tested the vapour load on the first two types of mixtures. So, it will be interesting to see if the findings of Porter & Momoh[15] still stand for non-ideal mixtures.

4.4.2 Number and notation of possible sequences

The equation that gives number of possible sequences as a function of the number of components is derived by King [9]:

$$N_{sequences} = \frac{[2(N_{comp}-1)]!}{N_{comp}!(N_{comp}-1)!} \tag{4.26}$$

As only mixtures with five components are used, from the equation is calculated that 14 different sequences are possible. In order to create a short notation, the sequences are numbered as presented in Table 4.2. The letters A, B, C, D and E refer to the notation given in the first column of Table 4.1.

Table 4.2: The numbering of the sequences

No.	Column 1	Column 2	Column 3	Column 4
1	A+BCDE	B+CDE	C+DE	D+E
2	A+BCDE	B+CDE	CD+E	C+D
3	A+BCDE	BC+DE	B+C	D+E
4	A+BCDE	BCD+E	B+CD	C+D
5	A+BCDE	BCD+E	BC+D	B+C
6	AB+CDE	A+B	CD+E	C+D
7	AB+CDE	A+B	C+DE	D+E
8	ABC+DE	A+BC	B+C	D+E
9	ABC+DE	AB+C	A+B	D+E
10	ABCD+E	ABC+D	AB+C	A+B
11	ABCD+E	ABC+D	A+BC	B+C
12	ABCD+E	AB+CD	A+B	C+D
13	ABCD+E	A+BCD	BC+D	B+C
14	ABCD+E	A+BCD	B+CD	C+D

4.5 Results & Discussion

4.5.1 Calculation of the relative volatility

For the calculation of the different relative volatilities the Antoine's equations were used. In general the Antoine's equation is given as:

$$\log P^{sat} = A^{Ant} - \frac{B^{Ant}}{T + C^{Ant}} \tag{4.27}$$

The temperature is given in °C and the pressure in mmHg. For the different components the A^{Ant}, B^{Ant} and C^{Ant} are found in the Dechema Chemistry Data Series[6] and in Hirate et al.[8]. The values are given in appendix 10.4. With equation

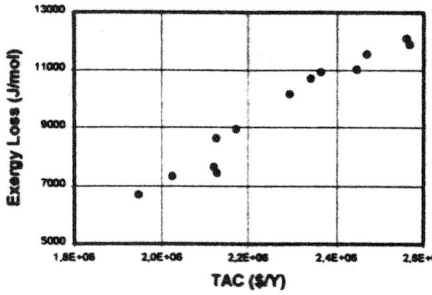

Figure 4.2 : Ideal exergy loss vs. TAC of mixture 1

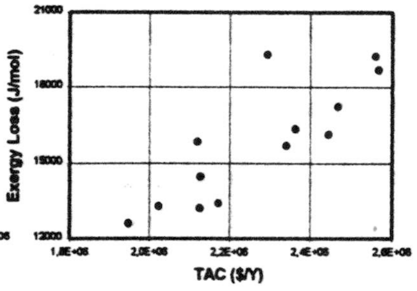

Figure 4.5 : Non-ideal exergy loss vs. TAC of mixture 1

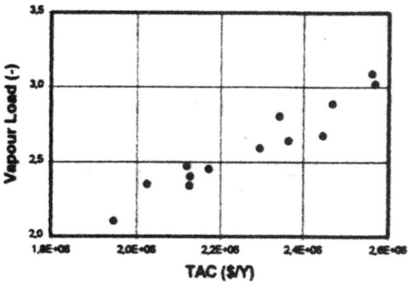

Figure 4.8 : Vapour load vs. TAC of mixture 1

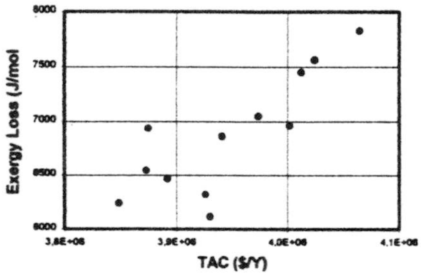

Figure 4.3 : Ideal exergy loss vs. TAC of mixture 2

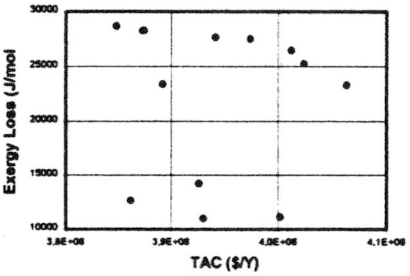

Figure 4.6 : Non-ideal exergy loss vs. TAC of mixture 2

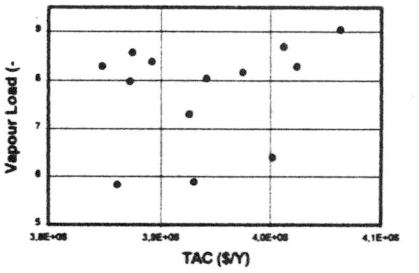

Figure 4.9 : Vapour load vs. TAC of mixture 2

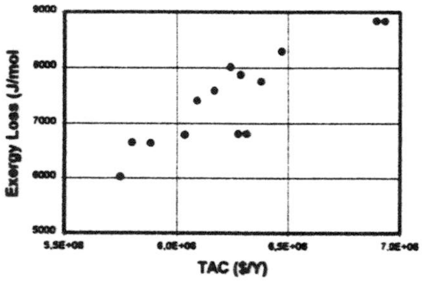

Figure 4.4 : Ideal exergy loss vs. TAC of mixture 3

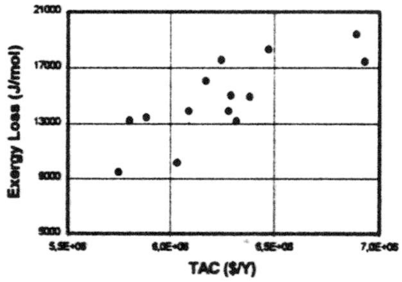

Figure 4.7 : Non-ideal exergy loss vs. TAC of mixture 3

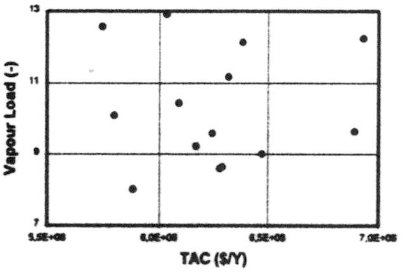

Figure 4.10 : Vapour load vs. TAC of mixture 3

(4.8) and this Antoine's equation the relative volatilities are calculated. These results are presented in Table 4.3.

Table 4.3: relative volatilities

	Mixture 1		Mixture 2		Mixture 3	
	Components	α	Components	α	Components	α
A	n-pentane/ n-hexane	3.10	propane/ i-butane	2.00	ethanol/ i-propanol	3.23
B	n-hexane/ n-heptane	3.13	i-butane/ n-butane	1.33	i-propanol/ n-propanol	1.11
C	n-heptane/ n-octane	2.91	n-butane/ i-pentane	2.40	n-propanol/ i-butanol	1.62
D	n-octane/ n-decane	14.7	i-pentane/ n-pentane	1.25	I-butanol/ i-butanol	2.42

Here the previously mentioned characters of the three mixtures become obvious. Mixture 1 is highly ideal and has easy separations ($\alpha > 2$). Mixture 2 is also ideal but has two difficult separations ($\alpha < 1.5$). Mixture 3 is not very ideal due to the polarity of the alcohols and has one difficult separation.

Instead of the relative volatilities, the non-ideal exergy loss needs the enthalpies of vaporisation. These are found in the Handbook for Chemistry and Physics [7]. These values are presented in appendix 10.3.

4.5.2 **Comparison of the criteria with graphs**

In order to compare the criteria with the Total Annual Cost, the TAC is put on the x-axis and the criterion on the y-axis for all three mixtures and all three criteria. So, this gives nine graphs in total. Figures 4.2, 4.5 and 4.8 show the results for mixture 1. It is clear that both the vapour load and the ideal exergy loss predict the TAC better than the non-ideal exergy loss due to a better correlation of the points. This behaviour can also be seen in figure 4.3, 4.6 and 4.9, where the results for mixture 2 are shown. Only here the vapour load does not perform so well as the ideal exergy loss. For mixture 3 figure 4.4, 4.7 and 4.10 represent the results. Again the ideal exergy loss predicts the TAC very well. But for this mixture the non-ideal exergy loss is better than the vapour load. All the values of the criteria and the TAC presented in these figures can be found in appendix 10.5.

4.5.3 **Comparison the criteria with regression**

These conclusions of the previous subchapter are made with the bear eye. So, a quantification is necessary for solid conclusions. For this quantification of the behaviours of the criteria, a linear relation ship between TAC and the criteria is assumed as optimal situation. And this is justified taking the general course of the relation between the criteria and the TAC from the graphs. So, the regression is a measure for the predictive power of the criterion. Flowers[5] has also splitted up the TAC into annual costs for equipment, steam(used for heating) and brine(used for cooling). For these costs also a linear regression is performed in order to look which aspect of the costs contribute the most to the predictive power of the criterion. Table 4.4 gives the results of all these regressions.

Table 4.4: The regressions of the criteria

	Mixture 1			Mixture 2			Mixture 3		
	Ideal Exergy	Non-ideal Exergy	Vap. Load	Ideal Exergy	Non-ideal Exergy	Vap. Load	Ideal Exergy	Non-ideal Exergy	Vap. Load
TAC	0.960	0.733	0.932	0.742	0.038	0.061	0.803	0.610	0.001
Equipment	0.875	0.626	0.809	0.535	0.316	0.446	0.382	0.509	0.057
Steam	0.941	0.756	0.949	0.436	0.272	0.002	0.900	0.593	0.009
Brine	0.947	0.754	0.950	0.436	0.272	0.002	0.861	0.510	0.021

The conclusions drawn from only looking at the graphs are affirmed. The regressions of the TAC show that the ideal exergy loss is the best criterion in all three mixtures, but its performance is not very good for mixture 2 and 3 mixture. For mixture 2 the other two criteria do not satisfy at all and for mixture 3 the non-ideal exergy loss shows a bit of linearity. So, it can be said for these mixtures that if there are more than two difficult separations ($\alpha < 1.5$), only the ideal exergy loss can be used and with only one difficult separation the non-ideal exergy loss can also be useful.

From the regressions of the annual equipment costs, annual steam costs and annual brine costs, no striking conclusion can be made. None of the parts show a significant better linearity than the others.

4.6 Conclusions

The most striking conclusion is that the ideal exergy criterion has a far better predictive power than the more accurate non-ideal exergy criterion. As expected, the vapour load is worse than both exergy criteria due to its weaker fundamental basis. So, more accurate equations do not always lead to better results! It can be expected that more accurate equations (for example with activity coefficients) will also not lead to better results. But more research should be done to prove this.

It is quite strange to conclude that the predictive power of the ideal exergy criterion versus the TAC is better than versus the components of the TAC while the other two criteria do not show this behaviour. An explanation can be that only in the equation for the ideal exergy criterion two different kinds of error are intrinsically present which compensate each other. It could be that by removing the assumptions (see chapter 4.2.3) in the derivation of the non-ideal exergy loss, this has also removed (a part of) this compensation. And this is probably the only reasonable explanation for the fact that the ideal exergy loss has a better predictive power than the non-ideal exergy loss

The contribution of this all is that a lot of time can be saved. If one wants to determine the most optimal sequence of distillation columns, a small calculation with the equation for the ideal exergy loss reduces the number of possibilities enormously. For example, from the 14 different sequences for 5 components, at least 11 sequences can be left out and this leaves only 3 sequences for rigorous calculations.

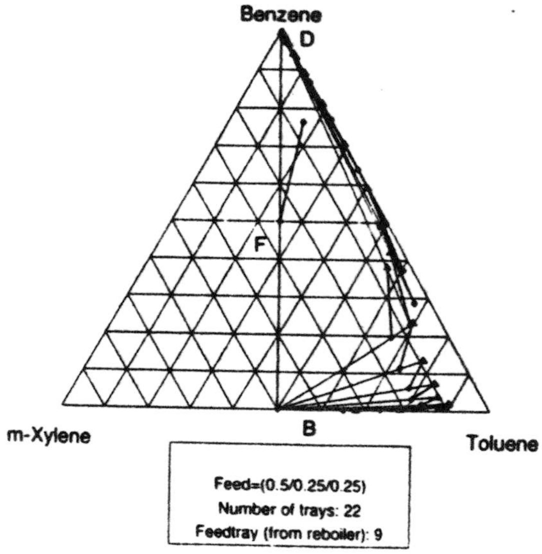

Figure 5.1 : McCabe-Thiele triangle with the feed at the 9th tray

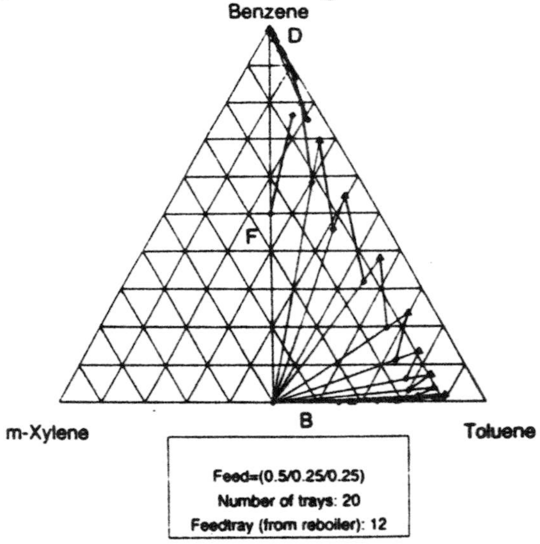

Figure 5.2 : McCabe-Thiele triangle with the feed at the 12th tray

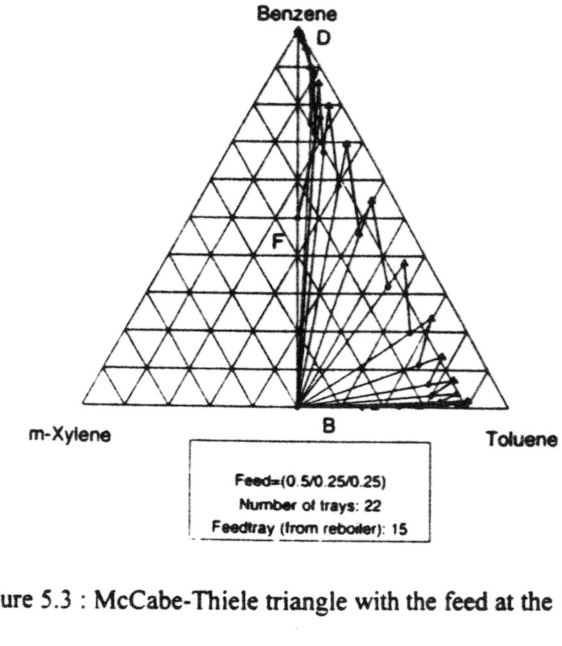

Figure 5.3 : McCabe-Thiele triangle with the feed at the 15th tray

5. Feed tray/ number of trays

5.1 Introduction

Besides the reflux ratio, the number of trays is the most important variable when a distillation column is designed. But these two variables are also directly dependant on each other. For two columns with the same separation performance but with another amount of trays, the column with the most trays has a smaller reflux ratio. In fact, the number of trays increases exponentially with decreasing reflux ratio. At minimum reflux ratio an infinite number of trays is necessary. The most common way to calculate this minimum reflux ratio is with the Underwood equations and is described already in chapter 3.5. The actual reflux ratio is obtained by the multiplication of the minimum reflux ratio and a factor, the necessary number of trays is also fixed.

So, the number of trays is in first instance determined by the reflux ratio. But the number of trays is also related to the feed tray. It can be imagined that an optimal feed tray exists. So, the minimum number of trays at given reflux ratio can only be reached with a correct location of the feed tray. The question is now how can this optimal feed tray be determined. Various variables can be suitable and this chapter will discuss three of them. All the simulations in this chapter are of course done with the C-program.

5.1.1 Example

First of all the existence of an optimal feed tray will be illustrated by an example. For this example a separation of benzene from toluene and m-xylene is simulated with the same separation performance but with different feed trays. The feed is 100 mole/s and the mole fractions of the feed are 0.50, 0.25 and 0.25 of respectively benzene, toluene and m-xylene. The reflux ratio is 4.972 while the distillate and bottom recoveries are specified as 0.999. The feed trays for this example are 9, 12 and 15 counted from the reboiler and the mole fraction triangles are given in figure 5.1, 5.2 and 5.3. It is clear for this case that entering the feed at tray 12 is the best of the three because the number of trays is less than the other two.

An explanation for this phenomenon is that if the feed is too high the highest trays in the stripping section do not perform significant separation compared to the lower trays. So these trays can better be added to the rectifying section where they can perform more separation so that fewer trays are necessary. And if the feed is too low the reverse takes place: the lowest trays in the rectifying section do not perform significantly and can better be used in the stripping section.

5.1.2 Minimum number of trays at fixed reflux ratio

In this example the criterion is the number of trays, but it can also occur that the minimum number of trays (at a fixed reflux ratio) is the same for a few consecutive feed trays. So, there are a few positions of the feed tray which lead to the minimum number of trays. In order to distinguish between those locations, the mole fraction in the distillate is taken as a criterion if the calculation is done from the bottom upwards. This mole fraction can be used because inherently to the tray-to-tray method the mole fractions of only one product flow can be exactly the same as given specified. The other one can only be above or below a certain specification because the method is based on discrete equilibrium steps. So, the chance that such a discrete step will result in the exact value of the specifications is very small. And it is at this exact specified product flow where the calculation starts.

As all the simulations in this chapter are done from the bottom, the bottom mole fractions are exact the same as specified but the mole fraction of the light key benzene in the distillate will always be higher than the specified value of for example 0.999. As the most optimal feed tray uses the separation performances of the trays most optimally, this feed tray will give the highest value above this specified value. So, the distillate mole fraction will show a maximum value for the most optimal feed tray at the minimum number of trays at fixed reflux ratio.

The number of those optimal feed trays at minimum number of trays will be dependant on the reflux ratio. At low reflux ratios this number of optimal feed trays will be low because the flows in the column are low and thus very sensitive to changes. As the feed causes a relatively large change it will have drastic effects on the column configuration. This sensitivity will decrease with increasing reflux ratio and the number of columns with the minimum number of trays will increase with it. This occurs until a certain point when the column becomes too small. And the number of optimal feed trays is limited due to the number of the total trays. So there should be a reflux ratio where the number of columns with the minimum number of trays has a maximum and is therefore also the most flexible reflux ratio.

5.1.3 Shortcut calculation

The usual calculation method for calculating the number of trays and feed tray locations is based on a few equations. These equations are mainly used for a shortcut calculation of which the results are used for a more rigorous calculation method.

For the feed tray location Kirkbride (Coulson&Richardson[1], page 422] has developed an empirical equation:

$$\log\left[\frac{N_{rect}}{N_{strip}}\right] = 0.206\log\left[\left(\frac{B}{D}\right)\left(\frac{x_{F,HK}}{x_{F,LK}}\right)\left(\frac{x_{B,LK}}{x_{D,HK}}\right)^{2}\right] \qquad (5.1)$$

The disadvantage of this equation that it does not give the number of trays in the stripping section or rectifying section but only their ratio. So the total number of trays should be calculated with another equation The Fenske's equation is frequently used for the calculation of the minimum number of trays (Coulson&Richardson[1], page 420):

$$N_{min} = \frac{\log\left[\dfrac{x_{LK}^{D}\, x_{HK}^{B}}{x_{HK}^{D}\, x_{LK}^{B}}\right]}{\log\alpha_{LK}} \qquad (5.2)$$

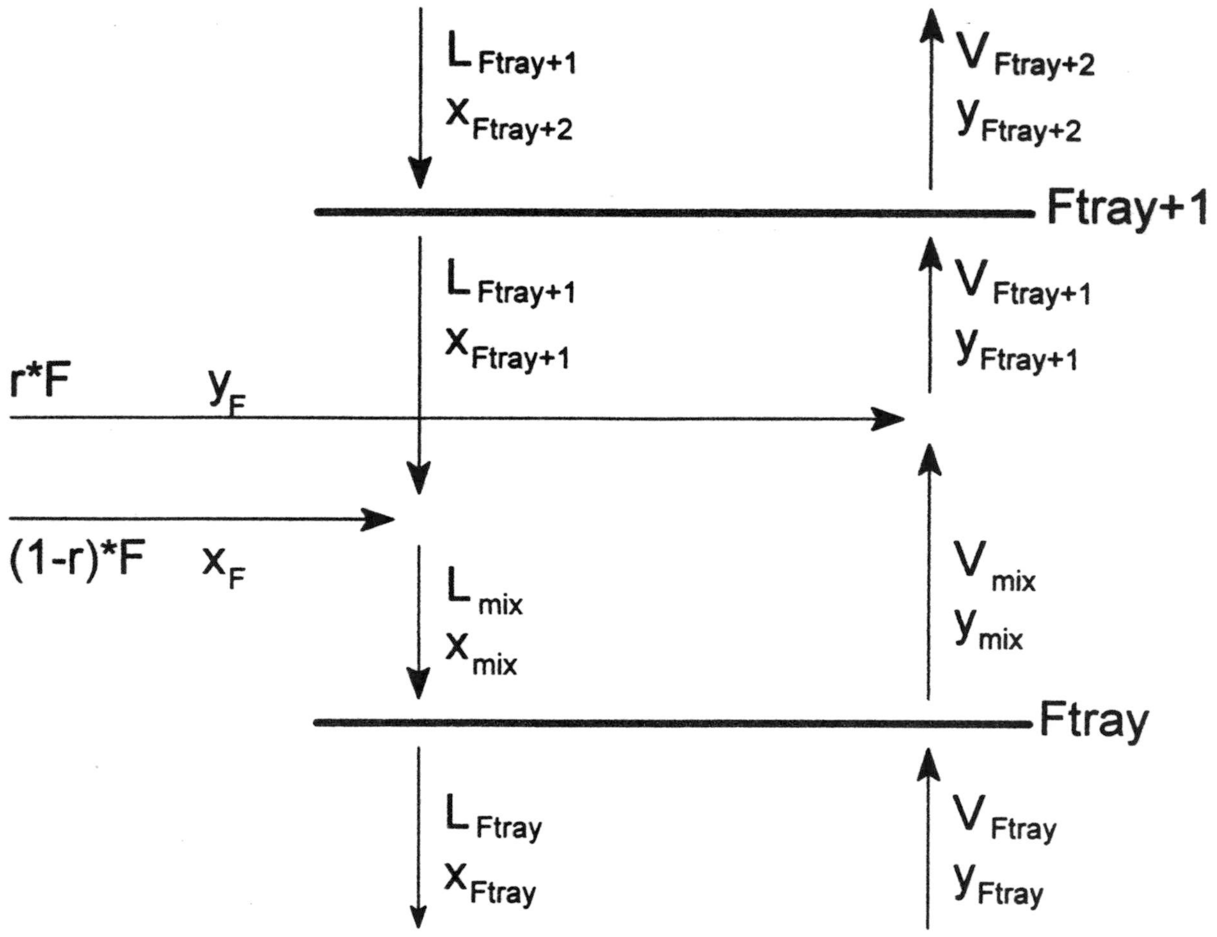

Figure 5.4 : Detail around the feed tray

The actual number of trays is given by Eduljee (Douglas[3] page 441):

$$\frac{N_{act} - N_{min}}{N_{act} + 1} = 0.75\left[1 - \left(\frac{R_{act} - R_{min}}{R_{act} + 1}\right)^{0.5688}\right] \tag{5.3}$$

The results of these equations will be compared with the results from the tray-to-tray method and the criteria for the feed tray location described in the following part.

5.2 **Criteria**

The entering of the feed has a large impact on the flows and mole fractions on the feed tray. Due to this large impact the entropy production and the exergy loss are high around the feed. So, all the criteria are based on the minimisation of the effects of the entering of the feed. It is believed that if these effects are minimal the separation performance of the trays around the feed is optimal. And the location of the feed tray at which this is the case, will give therefore the largest value for the benzene mole fraction in the distillate.

The criteria, which are in theory capable of minimising the effects of the entering of the feed, are given in the listing below:

1. Minimisation of the exergy loss due to mixing on the feed tray (see figure 5.4). The exergy loss due to mixing is given by the following balance:

$$\begin{aligned}\dot{Ex}^{loss} = {} & V_{mix} Ex^{vap}_{mix} + rFEx^{vap}_{F} - V_{Ftray+1} Ex^{vap}_{Ftray+1} + \\ & + L_{Ftray+1} Ex^{liq}_{Ftray+1} + (1-r)FEx^{liq}_{F} - L_{mix} Ex^{liq}_{mix}\end{aligned} \tag{5.4}$$

   As exergy has a solid fundamental basis, it is expected that this criterion will perform very well.

2. Minimisation of the entropy production rate of the system due to mixing on the feed tray. The same kind of balance as for the exergy loss gives the entropy production rate of the system due to mixing:

$$\begin{aligned}\Delta\dot{S}^{prod}_{sys} = {} & V_{Ftray+1} S^{vap}_{Ftray+1} - V_{mix} S^{vap}_{mix} - rFS^{vap}_{F} + \\ & + L_{mix} S^{liq}_{mix} - L_{Ftray+1} S^{liq}_{Ftray+1} - (1-r)FS^{liq}_{F}\end{aligned} \tag{5.5}$$

   As the exergy loss is largely determined by the entropy production rate of the system (see also equation 2.5 and 2.13), the difference between these two criteria should not be very large.

3. Minimisation of the temperature difference between the feed and the flow with which the feed is mixed:

$$\Delta T = (1-r)(T^{Ftray+1} - T^{Feed}) + r(T^{mix} - T^{feed}) \tag{5.6}$$

   This temperature difference will be in theory for the lowest feed trays negative and become positive for the higher feed trays (of course at minimum number of trays). And at the difference that is the closest to zero the optimal feed tray should be located according to this criterion. This is the easiest method because the calculation of the temperature profile is a standard operation in the rigorous simulation of distillation columns. So, this method is logically the most applied.

All the criteria are weighed according to the fraction vapour in the feed(r). As for all the analyses the vapour fraction of the feed is taken zero the r is also zero and this simplifies all these equations.

5.3 Results & Discussion

5.3.1 The different feeds and reflux ratios

The results are obtained from simulations with different feed mole fractions and reflux ratios. In engineering practice, these two variables are fixed due to process design and economic factors. The reason that they are varied here is purely for gaining more insight and accuracy. One of the insights is the number of columns with different feed trays that have the same minimum number of trays. The fixed parameters are the recoveries (0.999), the feed (100 mole/s), vapour percentage in the feed (0%) and the light key (benzene). Table 5.1 shows the values for the different feeds, reflux ratio, corresponding minimum number of trays and the number of columns with the minimum number of trays.

Table 5.1: feed mole fractions, reflux ratios , number of trays and number of columns with minimum trays

Feed mole fractions (benzene/toluene/m-xylene)	Reflux ratio	Minimum number of trays	Number of columns with minimum trays
0.70 / 0.15 / 0.15	9.924	19	2
	14.887	18	5
	17.368	18	5
	19.849	18	7
	24.811	17	4
0.50 / 0.25 / 0.25	4.972	20	2
	7.458	19	5
	9.944	18	5
	11.187	18	6
	12.430	18	6
	14.916	17	3
0.30 / 0.35 / 0.35	2.892	21	2
	4.338	19	3
	5.785	19	3
	7.231	18	5
	8.677	18	6
	10.123	17	3

From this table the statements made ratio in the theory about the behaviour at changing reflux are confirmed. The number of trays decreases indeed with the reflux ratio and the number of columns with a minimum number of trays increases first with

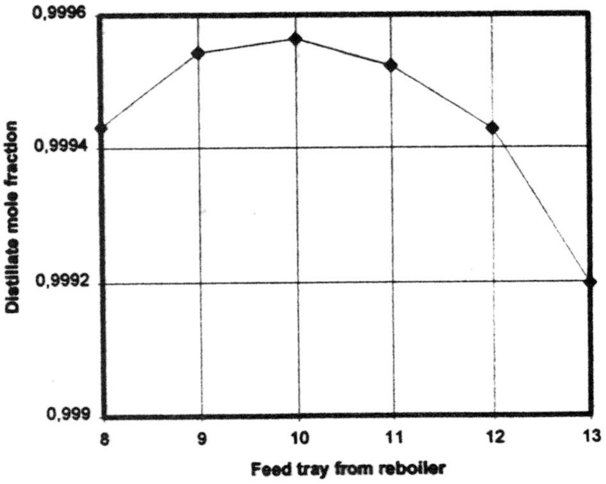

Figure 5.5 : The distillate mole fraction of benzene vs. the feed tray location

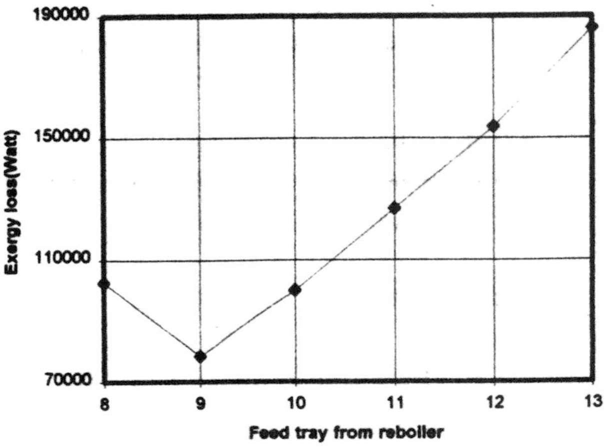

Figure 5.7 : The exergy loss due to mixing on the feed tray vs. the feed tray location

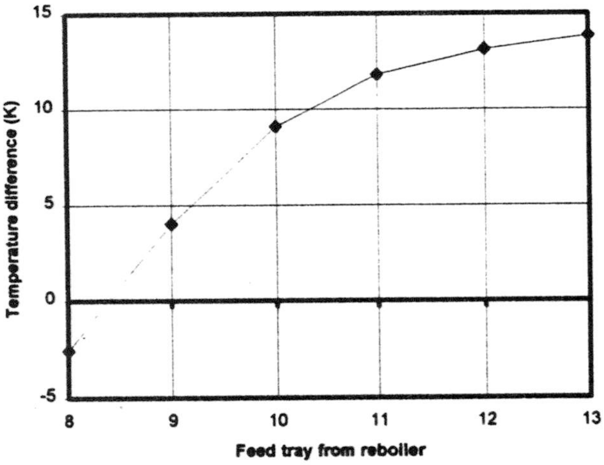

Figure 5.6 : The temperature difference of the flows which are mixed on the feed tray vs. the feed tray location

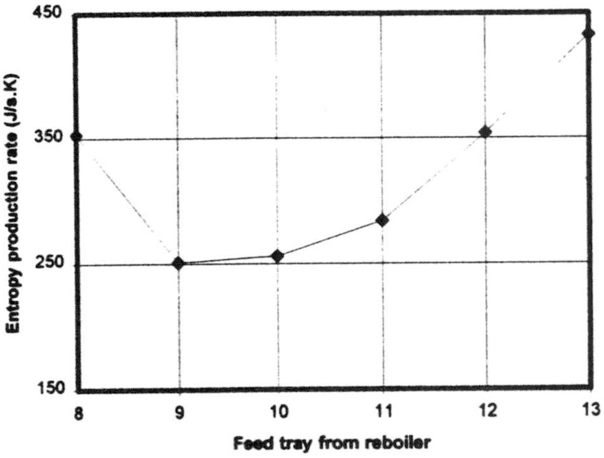

Figure 5.8 : The entropy production rate due to mixing on the feed tray vs. the feed tray location

increasing reflux ratio until a certain value and then decreases. It can also be seen that the reflux ratio increases with the benzene mole fraction in the feed at constant number of trays. This is explained by the dependency in the Underwood equations of the minimum reflux ratio on the mole fractions of the feed.

5.3.2 **Graphs**

As it would be too much to show all the results, only one combination of reflux ratio and feed mole fractions is given as a typical example. For this example the simulation of the 6 columns with consecutive fee tray locations. The reflux ratio is 12.430 and a feed mole fraction of benzene of 0.5 is taken. This example is chosen because it is one of the best results and it shows very clearly the general behaviour.

As already mentioned, the feed tray location is judged on the basis of the optimal value of the benzene mole fractions in the distillate. Figure 5.5 gives this deciding variable as a function of the feed tray. With this figure the three criteria will be compared. From this figure can be deduced that the entering the feed at tray 10 is the most optimal because it gives the highest value of the mole fraction. It should be mentioned that the values of the distillate mole fractions of benzene are very close to one and that the differences are very small. But the accuracy of these mole fractions is smaller than 10^{-5}. So, despite the small differences the course presented in this figure is accurate enough to base conclusions on. Taking this accuracy into account the entering of the feed at tray 9 or 11 can be considered almost equally optimal as the entering at tray 10 for this example.

The following figure 5.6 gives the temperature difference of the feed and the flow with which the feed is mixed as a function of the feed tray. The temperature difference has the smallest value closest to zero at feed tray 8. This does not correspond with the feed tray location given obtained from the benzene mole fraction in the distillate. So, here the first suspicion comes up that the temperature difference does not predict the optimal feed tray very well.

The exergy loss due to mixing as a function of the feed tray location is given in figure 5.7. A clear minimum can be observed at feed tray number 9. This is not the location given by the benzene mole fraction but it is already closer than the feed tray location pointed out by the temperature difference. But if the accuracy of the distillate mole fractions is taken into account, the exergy loss would give one of the three optimal feed trays and this is a good sign.

Figure 5.8 gives the entropy production rate due to mixing on the y-axis and the feed tray on the x-axis. The same kind of behaviour as for the exergy loss is observed. The optimal feed tray is at tray number 9. But the relative difference in entropy production rate between tray 9 and 10 is less than for the exergy loss. In fact the values of the entropy production rate are almost the same. So, a careful conclusion can be made that the entropy production rate predicts the optimal feed tray better than the exergy loss. And because the exergy loss is probably better than the temperature difference, the entropy production rate seems to be the best.

5.3.3 Quantification with regression

In order to quantify the predicting power of the different criteria, assumptions should be made about the relationship between the criteria and the benzene mole fraction in the distillate. If a criterion would predict the optimum feed tray perfectly, its function with the feed tray should have a maximum or minimum where the benzene mole fraction in the distillate has its maximum. But also the total behaviour presented in figures 5.6, 5.7 and 5.8 should correlate with the behaviour of the benzene mole fraction in the distillate in figure 5.5. In short terms a linear relationship between the and the benzene mole fraction in the distillate should be the most optimal situation. So, the regression can be taken (again) as a measure for the predictive power of the criterion. And these regression calculations are done for all the different feeds and reflux ratios, which have more than two columns with the minimum number of trays. If a regression is done for a relationship with only two points the regression would be one. All the regressions are given in appendix 10.6. The average of the regressions is taken of each of the three criteria as a final measure for the predictive power for the optimal feed tray. From these 14 regressions per criterion, also the standard deviation is calculated.

Table 5.2: Average regression and standard deviation of the feed tray analyses

	Temperature difference	Exergy loss	Entropy production rate
Average regression	0.165	0.497	0.651
Standard deviation	0.129	0.312	0.257

As the mean regression is a measure for the performance and the standard deviation is a measure for the reliability of the criterion, the conclusions are easy to draw. The temperature difference performs badly and should not be used! The exergy loss performs a lot better but its reliability is very weak. The best of the three is the entropy production rate: its mean regression is the highest and its standard deviation is high but still on the edge of acceptance. So, here the surprising result is obtained that the entropy production rate has a larger predictive power than the exergy loss. This is surprising because exergy loss should behave equally well.

One of the reasons for this bad predictive power of the exergy loss could be that exergy loss takes besides the entropy production also the enthalpy of mixing into account. And the entropy production rate of the system does not take this phenomenon into account. It could be that the thermodynamic model used is not able to calculate the heat of mixing correctly. The heat of mixing is given by the excess enthalpy, which is the difference between the real enthalpy of the mixture and the ideal enthalpy of the mixture. This enthalpy of mixing is given by the following equation for a liquid mixture(Smith and Van Ness [19]):

$$\Delta_{mix} H = H^E \qquad (5.7)$$

The entropy of an ideal mixture is dependent on the mole fraction via the ideal entropy of mixing. The entropy of mixing is given by:

$$\Delta_{mix}S = S^E - R\sum_{1}^{i} x_i \ln x_i \tag{5.8}$$

It could be that the entropy has a smaller relative deviation due to this extra dependence on the mole fractions, i.e., the inherent error of the thermodynamic model is covered.

A second reason for this discrepancy could be the assumption that the mixing of the two saturated liquids results in the same amount of an also saturated liquid (and that the mixing of two condensing vapours leads to the same amount of a condensing vapour). In reality a part of the mixture could evaporate or condense due to heat effects. These effects are assumed to be small and are not taken into account as already mentioned in chapter 3.2.5. This assumption introduces an inherent error in both the exergy loss and entropy production rate. But the exergy loss could be more sensitive for this error than the entropy production rate.

5.3.4 Comparison of the simulations with the shortcut method

The first step of this comparison is the shortcut calculation of the ratio between the number of trays in the rectifying section and the number of trays in the stripping section with equation (5.1). As this ratio is not dependent on the reflux ratio the value is here only dependant on the mole fractions in the feed. Table 5.3 gives the values for the three different feeds.

Table 5.3: The ratio of the number of trays in the rectifying section and the number of trays in the stripping section for the three feeds with the Kirkbride equation.

Feed (benzene/toluene/m-xylene)	0.70 / 0.15 / 0.15	0.50 / 0.25 / 0.25	0.30 / 0.35 / 0.35
N_{rect}/N_{strip}	0.4591	0.6531	0.9239

The ratio increases with decreasing mole fraction of the light key benzene. This could be expected because, if the mole fraction in the feed of the light key is high, less separation is necessary in the rectifying section than if that mole fraction is low. So, also fewer trays are necessary. However, the stripping section needs more trays in this case with high light key mole fractions in the feed. So, the overall effect is as calculated.

The second step is to calculate the minimum number of trays at all the reflux ratios and feeds. But for these calculations the minimum reflux ratio and the relative volatilities are necessary. The relative volatilities are constant for each column because the specifications in the distillate and bottom do not change. Table 5.4 gives the values relative to the heavy key toluene.

Table 5.4: The relative volatilities

	Relative volatility
Benzene/Toluene	2.1244
M-xylene/Toluene	0.6869

The minimum reflux ratio only depends here on the feed mole fractions, just like the ratios in Table 5.3. Table 5.5 presents the results of the Underwood equations.

Table 5.5: The minimum reflux ratio for the three feeds.

Feed (benzene/toluene/m-xylene)	0.70 / 0.15 / 0.15	0.50 / 0.25 / 0.25	0.30 / 0.35 / 0.35
Minimum reflux ratio	2.357	1.468	1.106

Finally equations (5.2) and (5.3) are used for calculating the actual number of trays for all the reflux ratios and feeds. Together with the ratio of Table 5.3 the feed tray location is calculated. These results are presented together with the results of the simulation in order to make an easy comparison possible in Table 5.6.

Table 5.6: Feed mole fractions, reflux ratios , optimal feed tray and the minimum number of trays for the simulations and the shortcut method.

Feed mole fractions (benzene/toluene/ m-xylene)	Reflux ratio	Number of trays simulation	Optimal Feed tray simulation	Number of trays shortcut	Optimal feed tray shortcut
0.70 / 0.15 / 0.15	9.924	19	12	21	14
	14.887	18	11	20	14
	17.368	18	11	20	14
	19.849	18	11	20	14
	24.811	17	10	19	13
0.50 / 0.25 / 0.25	4.972	20	12	22	13
	7.458	19	11	21	13
	9.944	18	10	20	12
	11.187	18	10	20	12
	12.430	18	10	20	12
	14.916	17	10	20	12
0.30 / 0.35 / 0.35	2.892	21	12	24	12
	4.338	19	10	22	11
	5.785	18	10	21	11
	7.231	18	9	21	11
	8.677	18	9	20	11
	10.123	17	9	20	10

The first observation tells that the shortcut calculations give a larger number of trays than the simulated rigorous tray-to-tray calculations and that therefore also a higher feed tray is obtained. It could be concluded that the shortcut method is too safe in its estimates. But the shortcut method is in fact derived for binary distillation and extended for multi component distillation. So, it is likely that the inherent error in the shortcut method is quite large.

In order to make a fair comparison the ratios between the number of trays in the rectifying section and the number of trays in the stripping section are calculated. As this ratio is assumed not be dependant on the reflux ratio, the average ratio for the three feeds is taken and the results are presented in Table 5.7.

Table 5.7: The mean ratio of the number of trays in the rectifying section and the number of trays in the stripping section of the three feeds for the simulations.

Feed (benzene/toluene/m-xylene)	0.70 / 0.15 / 0.15	0.50 / 0.25 / 0.25	0.30 / 0.35 / 0.35
N_{rect}/N_{strip}	0.6385	0.7655	0.9178

From a comparison with Table 5.3 can be seen that the two ratios with the highest benzene mole fraction in the feed are higher for the simulation than those of the Kirkbride equation. So, again differences between the shortcut method and the tray-to-tray simulations are observed. And again these differences are due to the lack of good predictive power of the shortcut method. In short terms, the shortcut method should only be used for what it is attributable: making the first estimations.

5.4 Conclusions

The main conclusion is that the entropy production rate due to mixing on the feed tray predicts the optimal feed tray better for this kind of simulations than the exergy loss due to the same mixing and the temperature difference between the flows that are mixed. The exergy loss is the second best and is not so bad that it is useless. But it is striking that the temperature difference has no predictive power at all while a lot of feed tray analyses are based on it.

From a fundamental point of view it is not logic that the exergy loss performs so badly. The first reason for this phenomenon could be that the errors made by the thermodynamic model are expressed in a larger way than in the entropy production rate due to the incorporation of the heat of mixing. The second reason is that a too simplified model for the mixing on the feed tray is taken and that this simplification has a larger impact on the exergy loss results than on the entropy results. So, more research can be done on this topic. First of all the model of the mixing should be improved in order to check if the exergy loss still performs badly. But the mixing on the feed tray is perhaps not the performance determining phenomenon. So, also other optimisations based on other phenomena should be analysed. For example the separation performance on the feed tray or the conditions of the mixed flows.

The second conclusion is that the shortcut method should be used where it is meant for: giving a first rough estimate of the number of trays and feed tray location. In this case the shortcut method gave a too large number of trays and a too high location of the feed tray compared with the simulations resulting from the tray-to-tray calculations.

A phenomenon that came up in these analyses and deserves more attention is the fact that the number of possible feed trays with the minimum number of trays has a maximum at a certain reflux ratio. So, at this reflux ratio the column has the most flexible configuration with respect to the location of the feed tray. Perhaps this kind of behaviour is related to the total flexibility and maximum output of the column. But more research should be done to affirm this presumption.

6. Interstage heat exchangers

6.1 introduction

The aim is to develop a method for determining the exergetic optimal location of two interstage heat exchangers in a distillation column. This will be done with the aid of the principle of equipartition of forces and the irreversible thermodynamics. For economical reasons, only two heat exchangers are added: one in the stripping section and one in the rectifying section.

The use of irreversible thermodynamics is relatively unknown in engineering but its attention is increasing. Especially the equipartition of forces, which is based on the irreversible thermodynamics is according Sauar[17] and Kjelstrup Ratkje[10] a very promising tool with respect to finding the exergetic optimal process design, which is a typical engineering topic. As the addition of heat exchangers is a proved improvement of the design, this principle should be able to predict this improvement and therefore also the optimal locations of the heat exchangers.

6.2 Theory: Irreversible thermodynamics

6.2.1 Entropy production described with fluxes and forces

For the understanding of the principle of equipartition of forces, a brief introduction into irreversible thermodynamics is given. Irreversible thermodynamics describes the entropy generation rate as a sum of products of fluxes and forces:

$$\Delta\dot{S} = \sum_{1}^{k} J_k X_k \tag{6.1}$$

The fluxes(J_k) can be written as a sum of products of transport coefficients and forces, when the gradients are not too large:

$$J_k = \sum_{1}^{l} L_{kl} X_l \tag{6.2}$$

These transport coefficients will become important in the discussion about the principle of equipartition of forces.

The simulation with the C-program gives already the entropy production rate, the flows and mole fractions per stage based on balances and the UNIQUAC-Redlich-Kwong equation of state(see equation (3.31)). Also the molar and energy fluxes can be extracted. But the forces are not obtained directly. So, in order to develop a method for the location of interstage heat exchangers based on the principle of equipartition of forces, it is necessary to define an equation for the forces with the equations from the irreversible thermodynamics.

For the way distillation for three components is treated here, four forces are present: one thermal force based on the temperature difference and three molar forces based on the chemical potential. The main equation for the entropy production rate with 3 components on a plate is rewritten from equation (6.1):

$$\Delta\dot{S} = -J'_q \frac{\Delta T}{T^2} - \frac{1}{T}\sum_{i=1}^{3} J_i^{molar}\Delta\mu_{i,T} \qquad (6.3)$$

Usually one of the molar driving forces is eliminated by using the Gibbs-Duhem equation:

$$\left(\frac{\partial nG}{\partial P}\right)_{T,n} dP + \left(\frac{\partial nG}{\partial T}\right)_{P,n} dT + \sum_{i=1}^{3} x_i d\mu_i = 0 \qquad (6.4)$$

This elimination implies that if two molar forces are given in a three component system the third will be automatically given. The further implementation of this equation is rather complex and therefore not very surveyable. As an engineering tool is pursued, this equation is not used explicitly further. It is only used as a theoretical elimination of one molar force and is therefore the first simplification for the application of the principle of equipartition of forces.

6.2.2 Chemical potential

Here the first step is made towards the derivation of an equation for the chemical potential on a molar basis: the derivation of an equation for the chemical potential μ. This derivation can be found in Smith and Van Ness[19]. For an ideal gas mixture, the derivation is started with the Gibbs energy, enthalpy and entropy:

$$G^{ig} = H^{ig} - TS^{ig} \qquad (6.5)$$

$$H^{ig} = \sum y_i H_i^{ig} \qquad (6.6)$$

$$S^{ig} = \sum y_i S_i^{ig} - R\sum y_i \ln y_i \qquad (6.7)$$

If equation (6.6) and (6.7) are substituted into equation (6.5):

$$G^{ig} = \sum y_i G_i^{ig} + RT\sum y_i \ln y_i \qquad (6.8)$$

The chemical potential of species i in an ideal gas mixture is found by the application of:

$$\mu_{i,T}^{ig} = \left[G^{ig} - \sum_{h\neq i}\frac{\partial G^{ig}}{\partial x_h}\right]_{P,T,\hat{x}_h} \qquad (6.9)$$

After the differentiation, the following simple equation is found:

$$\mu_{i,T}^{ig} = G_i^{ig} + RT\ln y_i \qquad (6.10)$$

In a similar way the chemical potential of a species in an ideal solution can be derived:

$$\mu_{i,T}^{id} = G_i^{id} + RT\ln x_i \qquad (6.11)$$

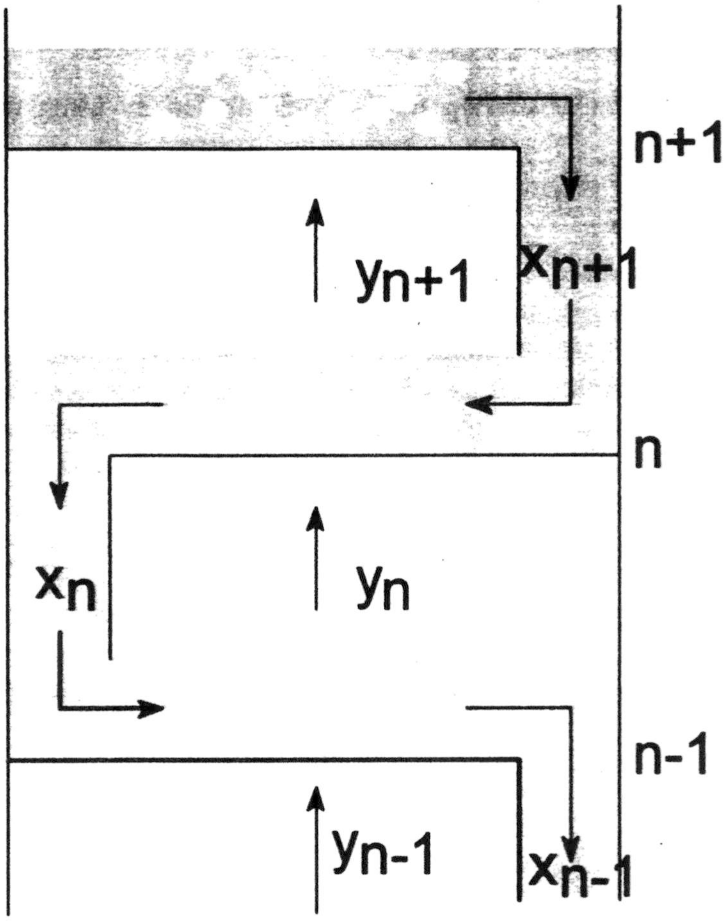

Figure 6.1 : Scheme of the mole fractions between a tray

6.2.3 **Mass force on a tray**

The question is now how to define the force on a tray, i.e., which difference in chemical potential should be taken. The derivation will be done with figure 6.1, which represents a scheme of the mole fractions between the trays. For understanding the next equations the numbering of the flows and mole fractions is very important.

The molar forces are defined as the difference in chemical potential between the mole fractions in the liquid and vapour on the tray. As the mole fractions are not constant on the tray due to the establishment of equilibrium during the stay on the tray, The average mole fraction are used. Figure 6.1 shows how the mole fraction in the liquid changes from x^{n+1} to x^n and in the vapour from y^n to y^{n+1} on tray no. n. But this average mole fraction does not take into account any assumptions about the concentration gradients or how the mixing occurs on the tray. It is a macroscopic view on the tray in which only the input and output are taken into account.

The incorporation of these changes, gives the following equations for the average chemical potential in the vapour on the tray:

$$\overline{\mu}_{i,T}^{vap} = G_i^{ig}(T,P) + R^{gas}T\ln\sqrt{y_i^n y_i^{n+1}} \tag{6.12}$$

And in the liquid:

$$\overline{\mu}_{i,T}^{liq} = G_i^{id}(T,P) + R^{gas}T\ln\sqrt{x_i^n x_i^{n+1}} \tag{6.13}$$

It should be mentioned that this macroscopic use of the average mole fraction is only justified because here theoretical stages are assumed, i.e. a total establishment of equilibrium on the trays. But if an efficiency is introduced, premises about the way the liquid and the vapour are mixed must be made. And these premises have a direct influence on which driving force limits the molar transport rate. This limiting driving force is then of course the force to deal with.

The difference of these chemical potentials is the compositional driving force:

$$\overline{\mu}_{i,T}^{vap} - \overline{\mu}_{i,T}^{liq} = G_i^{ig}(T,P) - G_i^{id}(T,P) + R^{gas}T\ln\sqrt{\frac{y_i^n y_i^{n+1}}{x_i^n x_i^{n+1}}} \tag{6.14}$$

This equation can be further simplified with the pressure dependence of the Gibbs energies:

$$G_i^{ig}(T,P) = G_i^{ig}(T,P_i^{sat}) + R^{gas}T\ln\frac{P}{P_i^{sat}} \tag{6.15}$$

$$G_i^{id}(T,P) \cong G_i^{id}(T,P_i^{sat}) \tag{6.16}$$

As on the tray equilibrium is assumed, the following equation is valid:

$$G_i^{ig}(T,P_i^{sat}) = G_i^{id}(T,P_i^{sat}) \tag{6.17}$$

Combining the last four equations gives:

$$\overline{\mu}^{vap}_{i,T} - \overline{\mu}^{liq}_{i,T} = R^{gas}T\ln\left[\frac{P}{P_i^{sat}}\sqrt{\frac{y_i^n y_i^{n+1}}{x_i^n x_i^{n+1}}}\right] \tag{6.18}$$

The introduction of Raoult's law:

$$P_i^{sat}x_i^n = Py_i^{n+1} \tag{6.19}$$

gives:

$$\Delta\mu_{i,T} = \overline{\mu}^{vap}_{i,T} - \overline{\mu}^{liq}_{i,T} = R^{gas}T\ln\left[\sqrt{\frac{\left(x_i^n\right)^2}{\left(y_i^{n+1}\right)^2}\frac{y_i^n y_i^{n+1}}{x_i^n x_i^{n+1}}}\right] \tag{6.20}$$

Finally the molar force becomes:

$$X_i^{molar} = \Delta\mu_{i,T} = \frac{1}{2}R^{gas}T\left[\ln\frac{x_i^n}{x_i^{n+1}} + \ln\frac{y_i^n}{y_i^{n+1}}\right] \tag{6.21}$$

The temperature in this equation is just like the mole fractions the average temperature on the tray. As this temperature is also occurs in the denominator before the summation of the molar part of equation (6.3), this temperature drops out.

In theory it is not necessary to calculate the contributions of all three molar forces due to the Gibbs-Duhem equation but the correct use of this equation was rather complex. And therefore all three molar forces will be calculated.

6.2.4 **Thermal force**

For the thermal force ($\Delta T/T^2$), the temperature difference between the incoming liquid(L_{n+1}) and incoming vapour(V_n) is taken (see figure 6.1) and for the denominator the equilibrium temperature is taken. So, the thermal force is relatively easy to derive:

$$X^{thermal} = \frac{\Delta T}{T^2} = \frac{T_{liq}^{n+1} - T_{vap}^{n}}{{T_{liq}^{n}}^{2}} \tag{6.22}$$

The temperature in the denominator can also be replaced by the vapour temperature of tray number n+1 (T_{vap}^{n+1}) due to the assumption of equilibrium on each tray. This equation is again based on a macroscopic view on the tray and it neglects therefore the temperature gradients.

6.2.5 **Mass and thermal fluxes**

The mass fluxes per stage is defined as the mass flow of one component which is added on one tray. The molar balance over the vapour flow on one tray gives:

$$J_i^{molar} = V^n y_i^n - V^{n+1}y_i^{n+1} \tag{6.23}$$

The liquid molar fluxes can be calculated similarly but the absolute values of these fluxes are due to the molar balance the same as the vapour molar fluxes.

The derivation of the thermal flux is a bit more complicated because it consists of two parts: one due to the Fourier heat conduction and one part due to the energy transport by the molar fluxes. And it is the flux due to the Fourier heat conduction that should be used in equation (6.3). In order to obtain this heat transfer the energy balance gives:

$$J'_{q,liq} + \sum_{i=1}^{3} J_i^{molar} H_i^{liq} = J'_{q,vap} + \sum_{i=1}^{3} J_i^{molar} H_i^{vap} \qquad (6.24)$$

As the heat conductivity in the vapour phase is assumed to be much smaller than in the liquid phase, the Fourier heat conduction in the vapour phase can be neglected. So, equation (6.24) is rewritten as:

$$J'_q = \sum_{i=1}^{3} J_i^{molar} \Delta_{vap} H_i \qquad (6.25)$$

If an interstage heat exchanger is added, an extra energy flow is added to the energy balance and will taken into account.

6.2.6 Entropy production due to mixing on the feed tray

The entropy production due to mixing on the feed tray is not given by a product of flux and force on an easy way but it is a very important phenomenon as pointed out in chapter 5. So, it should be added with an other set of equations. For this contribution the ideal entropy production due to mixing is taken:

$$\Delta\dot{S}_{mix}^{feed} = r\Delta\dot{S}_{mix}^{vap} + (1-r)\Delta\dot{S}_{mix}^{liq} \qquad (6.26)$$

For the mixing of the liquids, the entropy production rate is (see figures 5.4 and 3.2);

$$\Delta\dot{S}_{mix}^{liq} = L_{mix}\sum x_i^{mix}\ln x_i^{mix} - L_{Ftray+1}\sum x_i^{Ftray+1}\ln x_i^{Ftray+1} - rF\sum x_i^{F}\ln x_i^{F} \qquad (6.27)$$

The entropy production rate for the vapour flows;

$$\Delta\dot{S}_{mix}^{vap} = V_{Ftray+1}\sum y_i^{Ftray+1}\ln y_i^{Ftray+1} - V_{mix}\sum y_i^{mix}\ln y_i^{mix} - (1-r)F\sum y_i^{F}\ln y_i^{F} \qquad (6.28)$$

For the symbols is referred to figures 3.2 and 5.4.

6.2.7 A model based on irreversible thermodynamics

All these equations in this subchapter together with their assumptions can be considered as a model based on irreversible thermodynamics for this type of distillation. With this model it is now possible to calculate the entropy production rate with the irreversible thermodynamics from the simulation data. But this model must be checked on its usefulness, especially all the assumptions need affirmation. Otherwise it is not possible to use the principle of equipartition of forces for determining the optimal location of the heat exchangers. This check will be done by the comparison of the entropy production rates obtained by this model with the entropy production rates which are already known from the entropy balance(equation (3.31)) and the UNIQUAC-Redlich-Kwong equation of state. So, two different ways for calculating the same quantity but with a total other purpose will be compared and should show consistency. This consistency must be fulfilled in order to affirm the usefulness of the model based on irreversible thermodynamics.

The results of the entropy balance and UNIQUAC-Redlich-Kwong equation of state are theoretically better than the model based on irreversible thermodynamics because it contains regressed experimental constants, i.e. the interaction parameters. The error will also be very small because the mixture benzene, toluene and m-xylene is highly ideal. Besides, it is the only way available for checking the model based on irreversible thermodynamics.

6.3 Theory: Equipartition of forces

6.3.1 Introduction

In the last few years the discussion is going on about the question which principle leads to the most optimal ideal design for processes. A good principle should point out how the fluxes, forces and entropy production should be divided ideally over the total transport path, so that the design with the least exergy loss and entropy production is obtained. In the case of distillation this principle should point out which entropy, flux or force at which tray has which value so that the optimal division of the entropy, fluxes and forces is obtained for the most optimal design of the column. And the structure of the apparatuses should be built according to this division of entropy, fluxes and forces. But also the settings of the variables in the process determine largely the division of the entropy, fluxes and forces. For a distillation column the division of the entropy, fluxes and forces can be influenced by adding interstage heat exchangers and therefore this principle should give where the heat exchangers should be built but also the duty of that heat exchanger so that the optimal course of the fluxes and forces is obtained.

6.3.2 Definition

For a process with constant transport coefficients, Tondeur and Kvaalen[23] have shown that the entropy production rate should have a uniform distribution along the space and/or time variables of the process in order to create the optimal design. So, they said that in the ideal design of a column on each tray the same amount of entropy production has to take place. The key weak point of Tondeur and Kvaalen is that they assume the transport coefficients from equation (6.2) to be constant. Kjelstrup[10] has proved that this condition is not realistic for distillation, i.e. the transport coefficients differ per tray. If the coefficients are not constant, a logic sequel is to equipartitionate the forces instead of the entropy production rate. And this idea is called the principle of equipartition of forces and has shown to have some promising applications[10, 17 and 18].

The principle of equipartition of forces defines that *the driving forces should be equipartitioned over the different transport paths in order to minimise the total entropy production rate (Sauar [16]).*

The precise mathematical description of the principle can be found in Kjelstrup Ratkje [10] and Sauar[17].

6.3.3 Conditions

The application of this principle is only valid with two conditions. The first condition is that the sum of all the fluxes on each tray should be constant:

$$\sum_n J_n = \sum_n L_n X_n = \text{constant} \tag{6.29}$$

This condition means that the force must have the same equally distributed value in the parts of the column where no input or output of mass or energy takes place.

The second important condition is that the total transfer area should be constant when comparisons between different column designs are done. This area is dependant on various dimensional variables like tray diameter and gas velocity. As in chapter 2.4 the assumption is made that no dimension considerations are taken into account, the condition of constant area can be met for comparisons of columns with the same 'basic' design. But if the amount of trays, the feed tray or the number of heat exchangers are not the same a comparison based on this principle cannot be made. It is assumed here that the location and duty of the heat exchanger do not effect the transfer area significantly and that therefore this condition is approximately fulfilled. So, comparisons of columns with the same number of heat exchangers but different locations and duties are assumed to be possible. This assumption should of course be checked afterwards.

6.3.4 The equipartitioned course and values of the forces in distillation

For the case of three component distillation, four forces have to be considered for equipartitionating: the three mass forces and the thermal force. From the condition that the forces should be equally distributed for each part where the total fluxes are constant, it can be derived that at the feed tray the value of the forces should also change because mass is added. So, the forces in the stripping section and rectifying section have an other optimal value.

First the optimal values for the molar forces are derived. The value of the molar forces in the stripping section is simply calculated by taking the total force necessary to go from the bottom mole fractions to the feed mole fractions divided by the number of trays in the stripping section. This is written with an equation by:

$$\overline{X}^{\text{strip}}_{\text{molar},i} = \frac{R^{\text{gas}}}{N^{\text{strip}}} \ln\left(\frac{x_i^{B}}{x_i^{F}}\right) \tag{6.30}$$

And for the rectifying section the same kind of equation is derived but now it is taken from the feed mole fractions to the distillate mole fractions:

$$\overline{X}^{\text{rect}}_{\text{molar},i} = \frac{R^{\text{gas}}}{N^{\text{rect}}} \ln\left(\frac{x_i^{F}}{x_i^{D}}\right) \tag{6.31}$$

With the feed mass and energy are added. So, the thermal forces have also other values in the two sections. The mean thermal force in the stripping section is then given by:

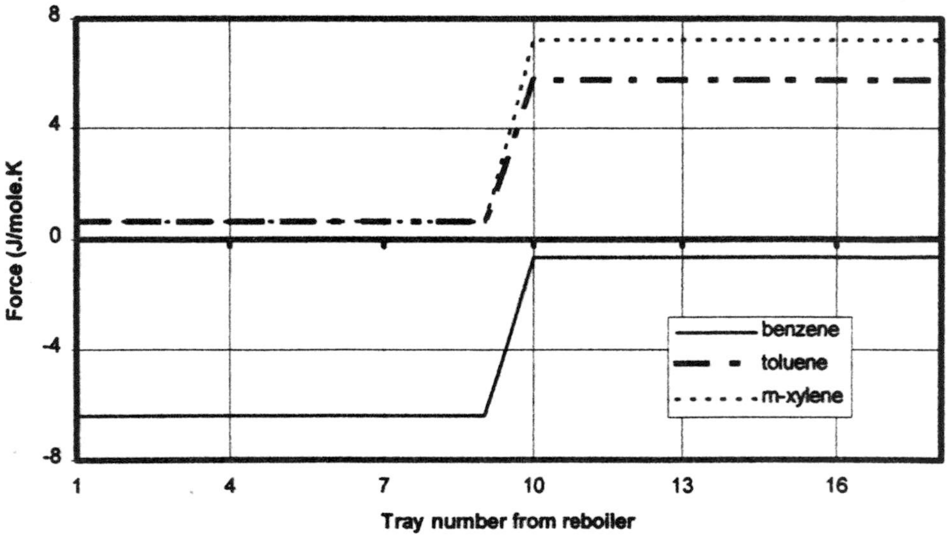

Figure 6.2: The ideal course for the mass forces according to the principle of equipartition of forces

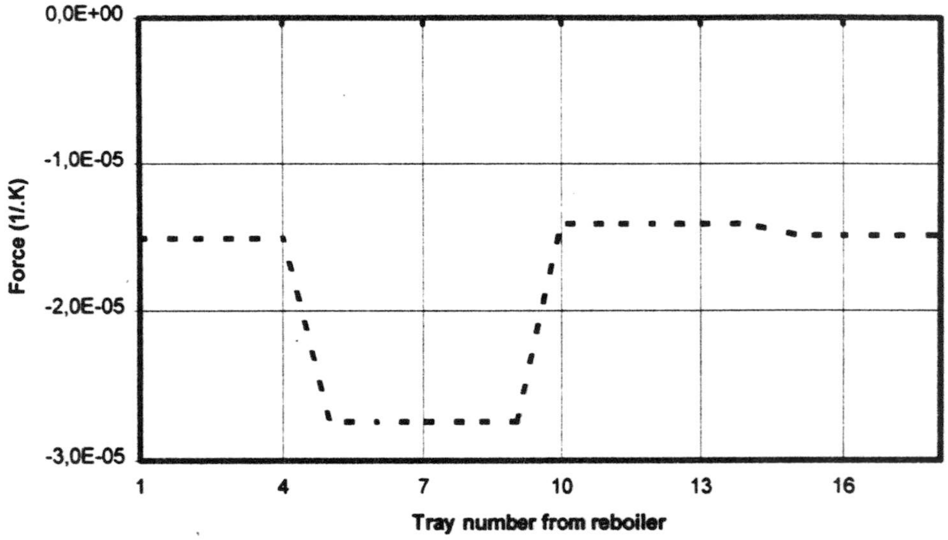

Figure 6.3 : Ideal course for the thermal forces according to the principle of equipartition of forces

$$\overline{X}^{\text{strip}}_{\text{thermal}} = \frac{1}{N^{\text{strip}}} \frac{T_{\text{feed}} - T_{\text{reb}}}{\left(\frac{1}{2}\left(T_{\text{reb}} + T_{\text{feed}}\right)\right)^2} \tag{6.32}$$

For the mean thermal force in the rectifying section:

$$\overline{X}^{\text{rect}}_{\text{thermal}} = \frac{1}{N^{\text{rect}}} \frac{T_{\text{cond}} - T_{\text{feed}}}{\left(\frac{1}{2}\left(T_{\text{cond}} + T_{\text{feed}}\right)\right)^2} \tag{6.33}$$

If one heat exchanger is added in the stripping section and on in the rectifying section, the column is divided due to the first condition into four parts with each a specific value for the thermal force.

For the part between the reboiler and the heat exchanger in the stripping section:

$$\overline{X}^{\text{reb-HX}}_{\text{thermal}} = \frac{1}{N^{\text{strip}}_{\text{HX}}} \frac{T^{\text{strip}}_{\text{HX}} - T_{\text{reb}}}{\left(\frac{1}{2}\left(T_{\text{reb}} + T^{\text{strip}}_{\text{HX}}\right)\right)^2} \tag{6.34}$$

For the part between the heat exchanger in the stripping section and the feed:

$$\overline{X}^{\text{HX-feed}}_{\text{thermal}} = \frac{1}{N^{\text{strip}} - N^{\text{strip}}_{\text{HX}}} \frac{T_{\text{feed}} - T^{\text{strip}}_{\text{HX}}}{\left(\frac{1}{2}\left(T^{\text{strip}}_{\text{HX}} + T_{\text{feed}}\right)\right)^2} \tag{6.35}$$

For the part between the feed and the heat exchanger in the rectifying section:

$$\overline{X}^{\text{feed-HX}}_{\text{thermal}} = \frac{1}{N^{\text{rect}}_{\text{HX}} - N^{\text{strip}}} \frac{T^{\text{rect}}_{\text{HX}} - T_{\text{feed}}}{\left(\frac{1}{2}\left(T_{\text{feed}} + T^{\text{rect}}_{\text{HX}}\right)\right)^2} \tag{6.36}$$

For the part between the heat exchanger in the rectifying section and the condenser:

$$\overline{X}^{\text{HX-cond}}_{\text{thermal}} = \frac{1}{N^{\text{total}} - N^{\text{rect}}_{\text{HX}}} \frac{T_{\text{cond}} - T^{\text{rect}}_{\text{HX}}}{\left(\frac{1}{2}\left(T^{\text{rect}}_{\text{HX}} + T_{\text{cond}}\right)\right)^2} \tag{6.37}$$

Note that only the optimal thermal forces and not the mass forces change at the heat exchangers because only energy is added and no mass.

The driving forces should be constant over the respective different parts of the column, and now the optimal course can be constructed. Figures 6.2 and 6.3 show an example of an optimal course for the forces of a distillation of benzene from toluene and m-xylene with the feed at tray 9 and the following feed, distillate, bottom mole fractions and temperatures as given in Table 6.1. The heat exchangers are at tray 4 and 11.

Table 6.1: Feed, distillate, bottom mole fractions and temperatures

	$x_{benzene}$	$x_{toluene}$	$x_{m\text{-}xylene}$	T(K)
Feed	0.5000	0.2500	0.2500	368.0
Bottom	0.0005	0.4995	0.5000	392.6
Distillate	0.9990	0.0010	0.0001	352.9
HX strip	-	-	-	383.5
HX rect	-	-	-	360.5

6.3.5 Possible differences from real processes

Of course the course of real processes will differ from the optimal course derived from the principle of equipartition of forces. So, the difference between the course of the real process and the course calculated with the principle can assumed to be a measure for the excess dissipation of the column. If this difference is really a measure for the excess dissipation, that difference should show correlation with the total exergy loss of a column. The question is now which difference will have the most correlation? The Gibbs-Duhem equation already eliminated one molar force for equipartitioning. So, two molar forces are left. In general the possibilities are:

1. The difference between one of the four real forces and the equally distributed course of this force. This would mean that only one force determines the correlation with total exergy loss.
2. The sum of the differences between the two of real molar forces and the thermal force and the equally distributed courses of these forces; If this is the case, all the forces should have an equal correlation with the total exergy loss. The third molar force is as already mentioned in theory given by the Gibbs-Duhem equation (equation (6.4)).
3. The sum of the differences between an other combination of the four real forces and the equally distributed courses of these forces than described in the second possibility; So, only a few forces would be determining for the total exergy loss. The other forces have in this case a constant contribution to the total exergy loss and have therefore no correlation.
4. The difference between the real force with the largest absolute value at each tray and the equally distributed course of this force; This would imply that not a specific force but only the largest one determines the correlation.
5. The difference between the key force and the equally distributed course of this force; This key force is the force which induces the main flux of interest. From the definition of the stripping section and rectifying section in chapter 2.2 can be said that the key force in the stripping section is the force of the light key and in the rectifying section the key force is the force of the heavy key.

Sauar[18] said that only the force related to flux of interest should be equipartitioned and the rest should be minimised. This statement implies that the fifth possibility would give the best correlation. But at this stage it is not possible to point out which of the possibilities will show the most correlation with the exergy loss with certainty. So, this must be decided on an empirical basis and will be discussed in the results.

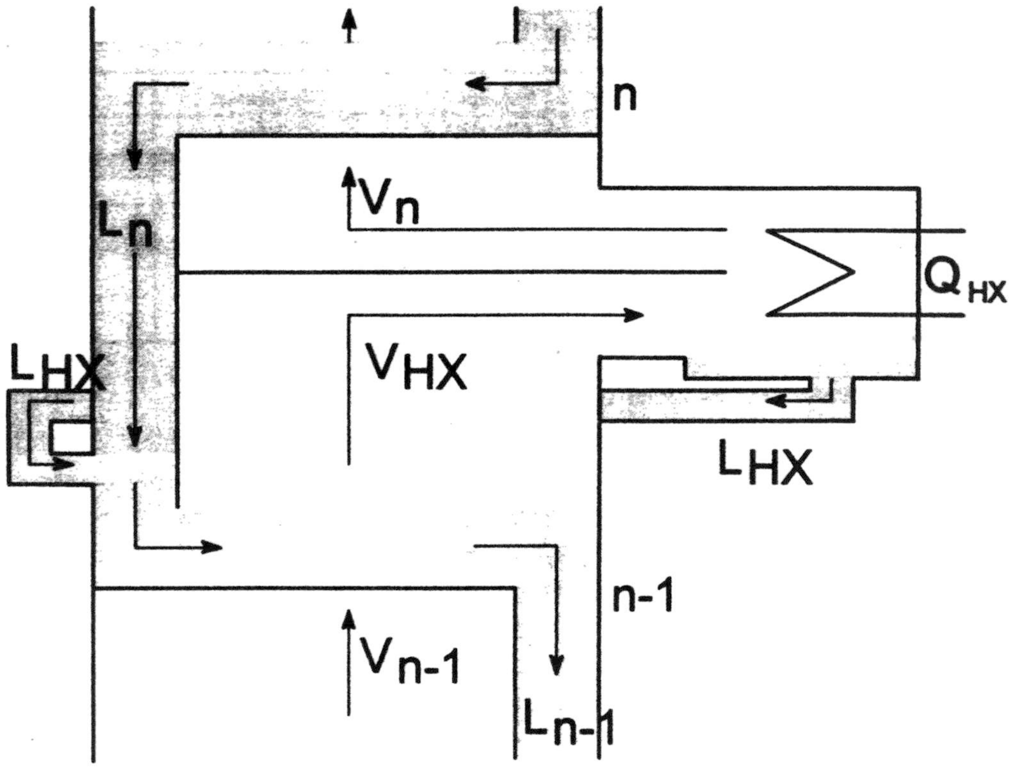

Figure 6.4 : Model for the heat exchanger in the rectifying section

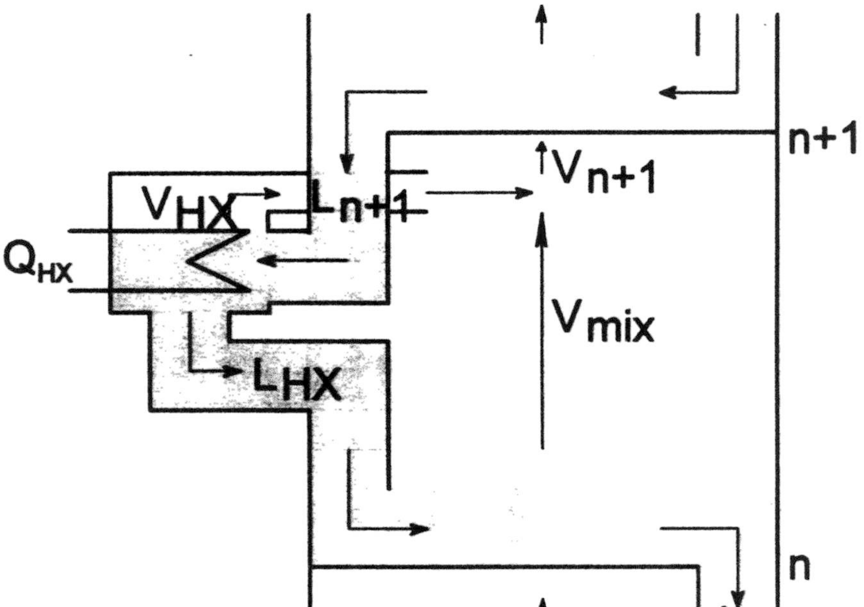

Figure 6.5 : Model for the heat exchanger in the stripping section

6.4 Model for the heat exchangers

6.4.1 Introduction

In order to obtain other (perhaps better equipartitioned) courses of the driving forces it is chosen as a practical option to add two heat exchangers: one in the stripping section and one in the rectifying section. This configuration has simply the most effect on the reduction of the exergy loss. It is not likely that more heat exchangers are economically viable because the decrease in exergy loss must cover the extra costs of building a heat exchanger. And it is not even sure that the addition of one heat exchanger is able to be profitable.

The addition of heat exchangers has large implications for the calculation method given in chapter 3. So, the choice of the model is very important. The heat exchanger in the rectifying section evaporates a part of the liquid flow and in the heat exchanger in stripping section condenses a part of the vapour flow. The model for those heat exchangers is presented in figure 6.4 for the rectifying section and 6.5 for the stripping section. It is assumed that the two flows leaving the heat exchangers are in equilibrium. These models are chosen because they are very effective due to this 'extra' equilibrium step beside the normal trays. An other important advantage was that these models were relatively easy to program. The necessary duties for the heat exchangers are obtained from the 'init.dat' file (see also appendix 10.8).

6.4.2 Heat exchanger in the stripping section

Based on these models, the following equations give the calculation method for both heat exchangers. First the heat exchanger in the stripping section will be treated. From the normal tray to tray calculation from the bottom the flows and mole fraction of L_{HX} and V_{mix} are known. The duty of the heat exchanger is also known. The first step is the estimation of the mean enthalpy of vaporisation based on the mole fraction in L_{HX}:

$$\Delta_{vap}\overline{H} = \sum x_i^{HX} \Delta_{vap} H_i \qquad (6.38)$$

The heats of vaporisation of the separate components are easily obtained from the interpolation function because it is able to give the enthalpy from both the liquid and vapour phase for the pure components.

Now, the L_n is calculated from the assumption that the duty is only used for vaporisation:

$$L_n = \frac{Q_{HX}^{strip} + \Delta_{vap}\overline{H} L_{HX}}{\Delta_{vap}\overline{H}} \qquad (6.39)$$

When a precise energy balance is made, it is deduced that the enthalpies of vaporisation in the denominator and numerator are different. But as the enthalpy of vaporisation is already an estimation, these two different enthalpies of vaporisation are also assumed to be the same.

So the vapour flow leaving the heat exchanger is:

$$V_{HX} = L_n - L_{HX} \qquad (6.40)$$

And the vapour flow going in tray number n:

$$V_n = V_{mix} + V_{HX} \tag{6.41}$$

As V_{HX} and L_{HX} are assumed to be in equilibrium with each other, the interpolation function gives the mole fractions in the vapour flow leaving the heat exchanger. Finally the mole fractions in L_n and V_n are calculated:

$$x_i^n = \frac{x_i^{HX} L_{HX} + y_i^{HX} V_{HX}}{L_n} \tag{6.42}$$

$$y_i^n = \frac{y_i^{mix} V_{mix} + y_i^{HX} V_{HX}}{V_n} \tag{6.43}$$

As the enthalpy of vaporisation is an estimation, the energy balance should be used to calculate the real duty of the heat exchanger:

$$Q_{HX}^{strip} = V_n H_n^{vap} + B H_B^{liq} - L_n H_n^{liq} - Q_{reb} \tag{6.44}$$

If this reboiler duty does not deviate more than 1% from the value used in equation (6.39), the calculation continues with the next tray. Otherwise, the duty is corrected and the calculation is done again until it is correct.

6.4.3 Heat exchanger in the rectifying section

The calculation procedure for the heat exchanger in the rectifying section is the same, but there are differences. From the normal calculations the mole fractions and flows of L_{mix} and V_{HX} are known. First the mean enthalpy of vaporisation is based on the liquid mole fractions with which V_{HX} is in equilibrium:

$$\Delta\overline{H}^{vap} = \sum x_{i,est}^{HX} \Delta H_i^{vap} \tag{6.45}$$

A subscript 'est' is added because these mole fractions will also be used for the first estimation of the mole fractions in the liquid flow leaving the heat exchanger.

The vapour flow leaving the heat exchanger is calculated with the assumption that the duty is used totally for condensation:

$$V_n = \frac{\Delta\overline{H}^{vap} V_{HX} - Q_{HX}^{rect}}{\Delta\overline{H}^{vap}} \tag{6.46}$$

When a precise energy balance is made, it is deduced that the enthalpies of vaporisation in the denominator and numerator are different. But as the enthalpy of vaporisation is already an estimation, these two different enthalpies of vaporisation are also assumed to be the same.

And the liquid flow leaving the heat exchanger:

$$L_{HX} = V_{HX} - V_n \tag{6.47}$$

As L_{HX} and V_n are assumed to be in equilibrium but the mole fractions of both are not known, an iterative procedure is necessary. As already mentioned, the first estimation of x_i^{HX} is obtained from an equilibrium with V_{HX}. So the first estimation for the mole fractions in V_n is made with:

$$y_{i,est}^{n} = \frac{V_{HX} y_i^{HX} - L_{HX} x_{i,est}^{HX}}{V_n} \tag{6.48}$$

The second estimation for the x_i^{HX} is obtained by the interpolation function due to the equilibrium. If this x_i^{HX} is the same as the previous estimation, the final mole fractions are obtained. Otherwise equation (6.48) and the interpolation technique are repeated with the new estimates for $x_{i,est}^{HX}$ until the final mole fractions are obtained. Again, the heat exchanger duty should be checked and corrected if it deviates more than 1% with repeating the previous calculation method. The energy balance is now:

$$Q_{HX}^{rect} = V_{n-1} H_{n-1}^{vap} - L_{n-1} H_{n-1}^{liq} - D H_D^{liq} - Q_{cond} \tag{6.49}$$

6.4.4 **Exergy loss and entropy production in the heat exchangers**

For the exergy of the heat transferred in the interstage heat exchangers the same equations as for the reboiler and condenser (equations (3.33) until (3.36)) are used. And also the same value of 5° C for the driving force is used. The entropy of the heat transferred in the heat exchanger in the rectifying section is given by:

$$\Delta \dot{S}_{HX,rect} = \frac{\dot{Q}_{HX,rect}}{T_{HX,rect} - \Delta T_{driv}} \tag{6.50}$$

The entropy of the heat transferred in the heat exchanger in the stripping section:

$$\Delta \dot{S}_{HX,strip} = \frac{\dot{Q}_{HX,strip}}{T_{HX,strip} + \Delta T_{driv}} \tag{6.51}$$

The exergy of the heat transferred in the heat exchanger in the rectifying section

$$\mathrm{E\dot{x}}_{\mathrm{HX,rect}} = \dot{\mathrm{Q}}_{\mathrm{HX,rect}} \left(1 - \frac{\mathrm{T}_0}{\mathrm{T}_{\mathrm{HX,rect}} - \Delta \mathrm{T}_{\mathrm{driv}}}\right) \tag{6.52}$$

The exergy of the heat transferred in the heat exchanger in the stripping section:

$$\mathrm{E\dot{x}}_{\mathrm{HX,strip}} = \dot{\mathrm{Q}}_{\mathrm{HX,strip}} \left(1 - \frac{\mathrm{T}_0}{\mathrm{T}_{\mathrm{HX,strip}} + \Delta \mathrm{T}_{\mathrm{driv}}}\right) \tag{6.53}$$

These exergies and entropies are added to the entropy balances and exergy balances at the corresponding trays.

These exergies and entropies are not used for the results from irreversible thermodynamics but only in simulations with UNIQUAC-Redlich-Kwong. For the irreversible thermodynamics the duty of the heat exchanger in the stripping section is added to the energy balance (see equation (6.24)). And the duty of the heat exchanger in the rectifying section is subtracted from that flux.

6.5 Results & Discussion: irreversible thermodynamics

6.5.1 Fixed specifications for the comparison

In order to examine the usefulness of the laws of the model based on the irreversible thermodynamics for the principle of equipartition of forces, two different columns are simulated: one with the heat exchangers and one without. So, the main effects of adding heat exchangers will also become clear. The necessary results are again obtained with a simulation of a separation of benzene from toluene and m-xylene. Table 6.2 gives the specifications, which are fixed during the analyses.

Table 6.2: Fixed specifications

$x^F_{benzene}$	0.50
$x^F_{toluene}$	0.25
$x^F_{m\text{-}xylene}$	0.25
Pressure (bar)	1.0
Recovery distillate	0.999
Recovery bottom	0.999
Number of trays	18
Feed tray (from reboiler)	9
Feed (mole/s)	100

6.5.2 Non-fixed specifications for the comparison

For this comparison the total energy demand of the two columns is taken equal. This means that the amounts of heat going into the stripping section and coming out the rectifying section are the same for the two columns. So, the heat put in the heat exchanger in the stripping section should be subtracted from the reboiler duty of the column without heat exchangers. And the heat coming out of the heat exchanger in the rectifying section should be subtracted from the condenser duty of the column without heat exchangers. So, the interstage heat exchangers just divide the heat better over the column. As the condenser duty is less due to the addition of the heat exchangers, the liquid flow coming down from the condenser is also less while the distillate flow remains the same. And therefore the reflux ratio is also less for a column without heat exchangers. So, the reflux ratio is in this case not a fixed specification.

The position of the heat exchangers is chosen around the feed at stage 8 and stage 10 and the duty of both heat exchangers is 3.0 MWatt. The reason for these locations could already be seen in chapter 3 in figures 3.4 and 3.5; the entropy production rate is simply the largest around the feed and changes at that place are expected to have the largest reducing effects. The choice for the duty is largely arbitrarily. It should not be too large and have therefore the size of the reboiler or condenser. And it should not be too small and have no observable effect. The value of 3 MW fulfils these conditions. It is around 20 % of the duties of the reboiler and condenser and it has an effect as will be shown later. So, besides the fixed specifications several specifications are different and these are given in Table 6.3.

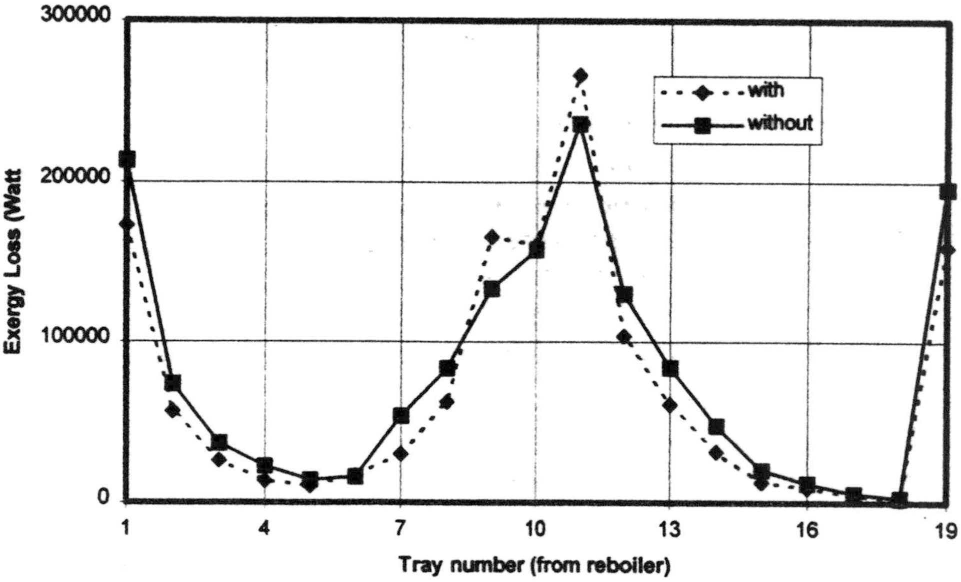

Figure 6.6 : Comparison of the exergy loss with and without heat exchangers obtained from the UNIQUAC-Redlich-Kwong simulations

Table 6.3: Non-fixed specifications

	Without heat exchangers	With heat exchangers
Reflux ratio	9.163	7.458
Reboiler duty (MWatt)	16.12	13.12
$Q^{HX,strip}$ (MWatt)	-	3.00
$Q^{HX,rect}$ (MWatt)·	-	3.00
Condenser duty (MWatt)	16.10	13.03

The difference in condenser duty is more than 3.00 MW due to different distillate mole fractions. The reason for this is already given in the feed tray analysis(chapter 5): it is inherently to the tray-to-tray calculation method. This phenomenon is not taken into consideration here because it is not significant compared to the effects of the heat exchangers.

6.5.3 **Reductions of exergy loss and entropy production rate**

Table 6.4 gives the exergy losses, entropy production rates of the columns with and without heat exchangers at tray 8 and 10. Also the reductions in exergy loss and entropy production rate of the addition of the heat exchangers relative to the column without the heat exchangers are presented. The exergy loss and entropy production rate include of course the contributions of the reboiler and condenser. Note that these entropy production rates are results from the C-program using the entropies and enthalpies obtained with the balances and the UNIQUAC-Redlich-Kwong equation of state and not yet from irreversible thermodynamics.

Table 6.4: Exergy loss, entropy production rate and reduction

	Without heat exchangers	With heat exchangers	Reduction
exergy loss (MWatt)	1.541	1.367	11.3 %
entropy production rate (J/s.K)	5167	4583	11.3 %

So, a large reduction can be obtained by adding heat exchangers. Knowing these reductions, an economical study should point out whether this reduction pays out the extra costs of the addition of the heat exchangers. And it is not so surprising that the reduction in entropy production rate and exergy loss are the same when no shaft work is done, because:

$$\dot{Ex}^{loss} = T_0 \Delta \dot{S}^{prod} \tag{6.54}$$

This comparison is also shown in figure 6.6 where for both columns the exergy loss per tray is shown. It is a bit surprising that the peak for the column with heat exchangers is slightly higher and that therefore at the bottom and top trays the reductions from Table 6.4 are achieved . So, the reduction is not obtained by the decrease of the peak around the feed but due to the reduction of the reboiler and condenser duties, i.e. the better distribution of heat!

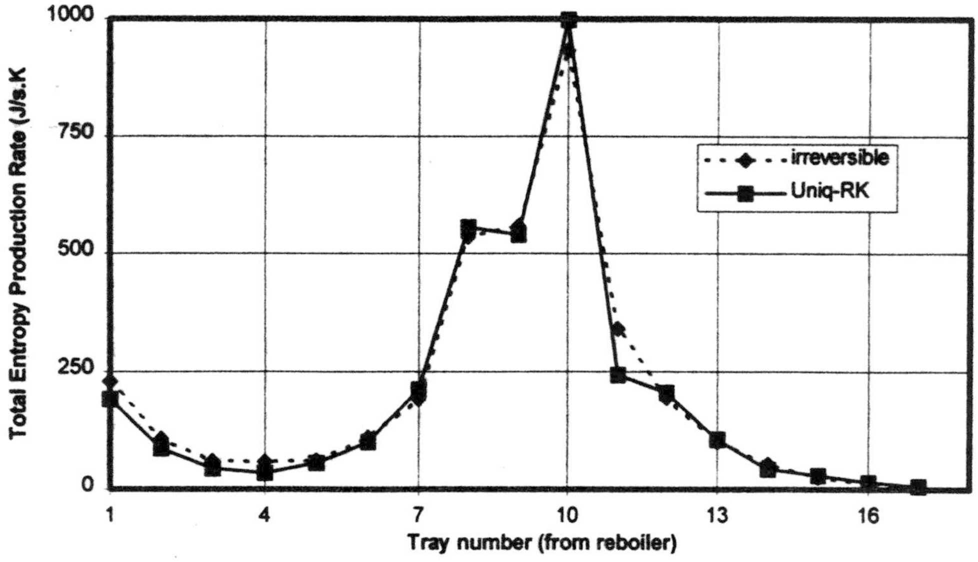

Figure 6.7: Comparison of the Uniq-RK with the irreversible thermodynamics with heat exchangers

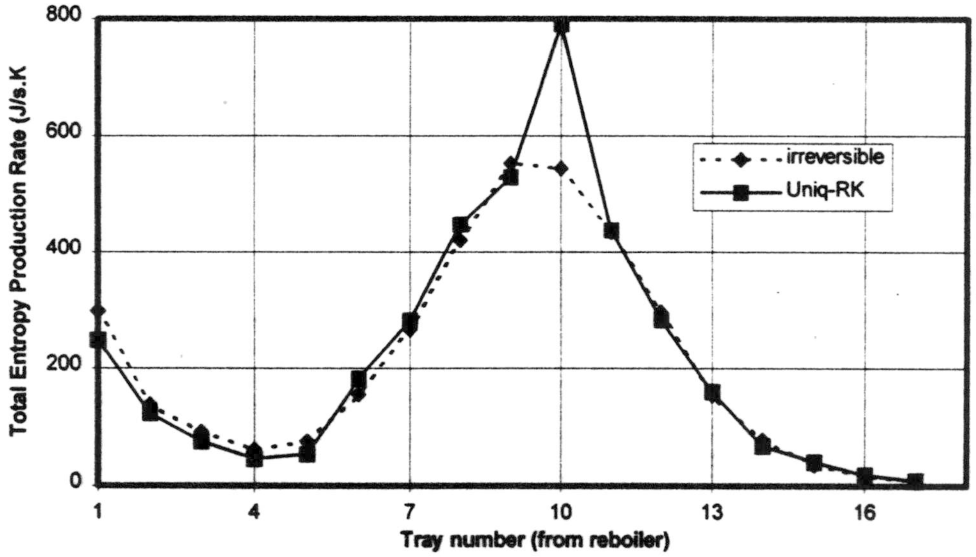

Figure 6.8 : Comparison of Uniq-RK with irreversible thermodynamics without heat exchangers

6.5.4 Usefulness of the irreversible thermodynamic laws

Now, the usefulness of the model based on the irreversible thermodynamics can be examined with these simulations. As a benchmark the entropy production rates calculated with the UNIQUAC-Redlich-Kwong equation of state are used together with the balances described in equation (3.31) and (3.32). And the results of the irreversible thermodynamics will be compared with it. As mentioned in subchapter 6.2.7, this comparison is the only reasonable way to check the assumptions which are made for the model based on irreversible thermodynamics. If the results coincides the model based on irreversible thermodynamics can be considered useful for this kind of distillation. Otherwise other assumptions have to be made in order to create a better model with irreversible thermodynamics.

For the calculations of the entropy production rates with the model based on irreversible thermodynamics, first the fluxes are calculated with equation (6.23) filling in the flows and mole fractions, which are results from the simulation. The mole fractions are also used for the calculation of the mass forces in equation (6.21). The temperatures are used to calculate the thermal forces with equation (6.22). Finally the entropy production rate is calculated with equation (6.3). A detailed description of the results of the calculations for the fluxes and forces can be found in appendix 10.7.

Figure 6.7 shows the comparison of the benchmark (the UNIQUAC-Redlich-Kwong equation of state with the balances of equation (3.31) and (3.32)) and the results from the model based on irreversible thermodynamics of the column with heat exchangers. And figure 6.8 gives the same for the column without heat exchangers. With the bare eye can already be concluded that the lines match quite well. A quantification of this resemblance is given with the calculation of the mean deviation percentages of the results of the model based on irreversible thermodynamics from the benchmark. Table 6.5 gives these mean percentages.

Table 6.5: The mean deviations from the benchmark

	mean deviation
without	12.9 %
with	16.8 %

So, in both cases the performance of the model based on irreversible thermodynamics is not bad at all. The fact that the column with heat exchangers is described worse is of course caused by the extra assumptions concerned the driving force in equations (6.50), (6.51) , (6.52) and (6.53). The calculation of the entropy production rate due to mixing on the feed tray with equation (6.26) causes also an error in comparison to the benchmark results. But it is still justified to use this model based on the irreversible thermodynamics for calculating the entropy production rates and this justification is the basis for using the principle of equipartition of forces.

6.5.5 Contributions of the different forces

Inherently to the use of the model based irreversible thermodynamics the contributions of the various forces can be calculated (see equation (6.3)). From the results presented in appendix 10.7, these contributions are calculated and given in Table 6.6.

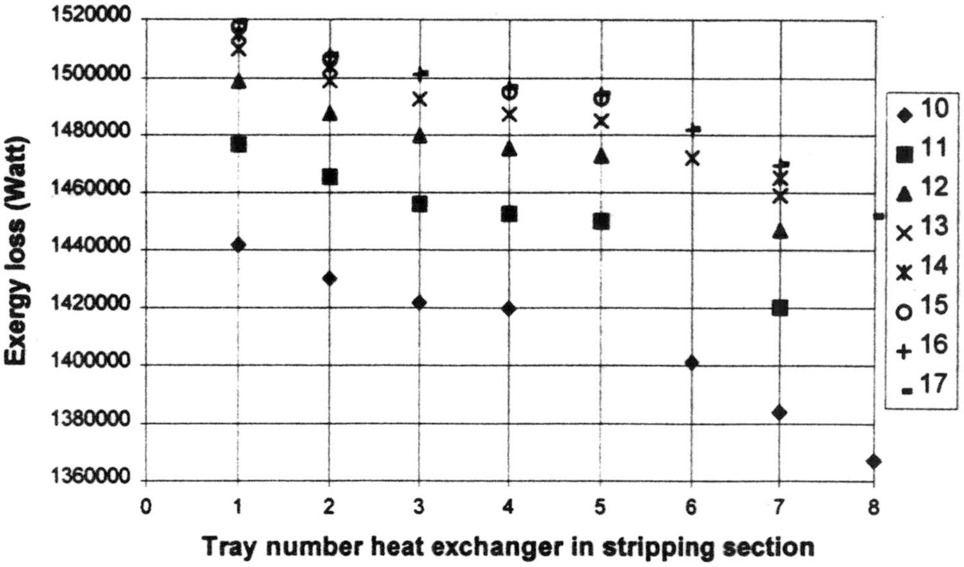

Figure 6.9 : Exergy loss of all combinations of positions of the heat exchangers

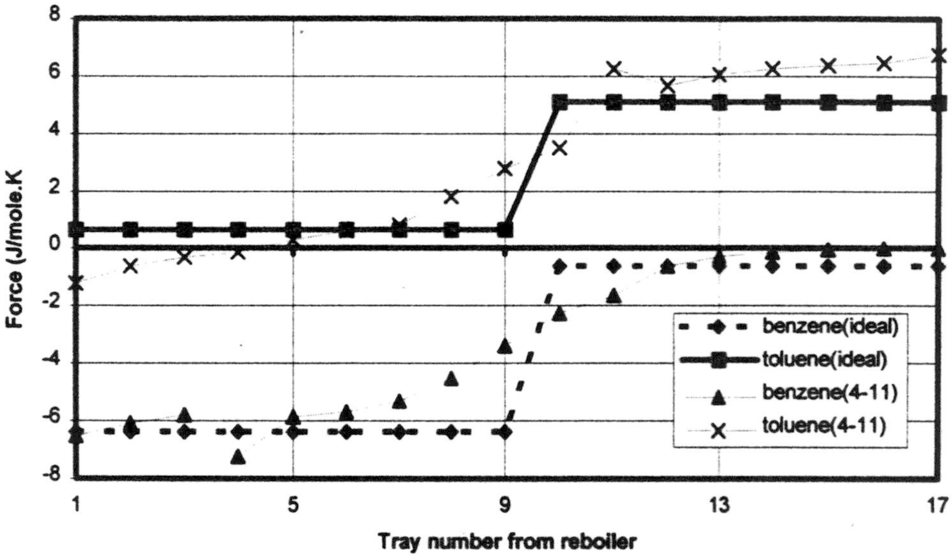

Figure 6.10 : The course of the forces of the light key benzene and the heavy key toluene of a simulation with heat exchangers on tray 4 and 11 together with the optimal forces resulting from the principle of equipartition of forces

Table 6.6: Contributions to the total entropy production rate

	without	with
Benzene	43.3 %	41.0 %
Toluene	40.8 %	37.4 %
M-xylene	15.1 %	12.5 %
Thermal	0.8 %	9.1 %

It is obvious that the contribution of the m-xylene forces and thermal forces are relatively small compared to the key forces. It could be that that the contribution of the thermal forces are depended on the difference in boiling temperature between the light and the heavy key. However, the assumption is made based on this that these small contributions can be left out in the further analyses with the equipartition of forces. So, only the light key and heavy key forces are taken into account. This assumption should be checked afterwards!

6.6 Results & Discussion: equipartition of forces

6.6.1 Exergy loss of all pairs of heat exchanger positions

The analysis of the principle of equipartition of forces is based on the same columns used for the justification of the use of the model based on irreversible thermodynamics. So, the values in Table 6.2 and Table 6.3 are used again. Only now all the possible positions of the heat exchangers are simulated. So, the results for all combinations of the position of the heat exchanger in the stripping section and in the rectifying section are obtained. The main results of these simulations are of course the total exergy losses of those columns. Figure 6.9 gives these exergy losses as a function of the position of the heat exchanger in the stripping section. The position of the heat exchanger in the rectifying section is given in this figure by different markers, which are given in the legend. Clearly, for both heat exchangers the exergy loss decreases when the positions move towards the feed. Finally, the assumption that changes around the feed will have the most effect is proved. It is also clear that the relation between the positions of the heat exchanger and the exergy loss is not linear for both sections. So, the decrease of the exergy loss with moving the heat exchangers towards the feed is not constant.

Unfortunately a few combinations of positions are missing. The reason for this absence is non convergence of either the iterations for the energy balance for a tray or the iterations for the equilibrium calculation in the heat exchanger in the rectifying section.

6.6.2 The possible deviations

From the equations (6.30) to (6.37) the optimal course of the forces according to the principle of equipartition of forces are constructed and presented in figure 6.10. Only the forces of the light key benzene and the heavy key toluene are given because previously is assumed that these forces are the determining ones. In this figure also the courses of the forces in a simulated column are given with a thin dashed line. The column has its heat exchanger in the stripping section on tray 4 and its heat exchanger

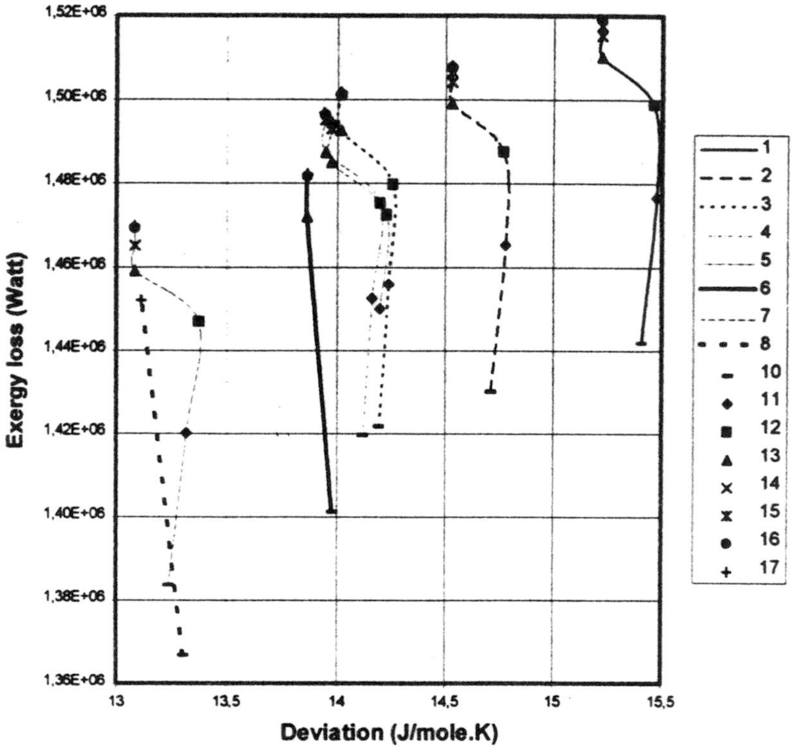

Figure 6.11 : Exergy loss vs. deviation of the heavy key (toluene) forces from the optimal course

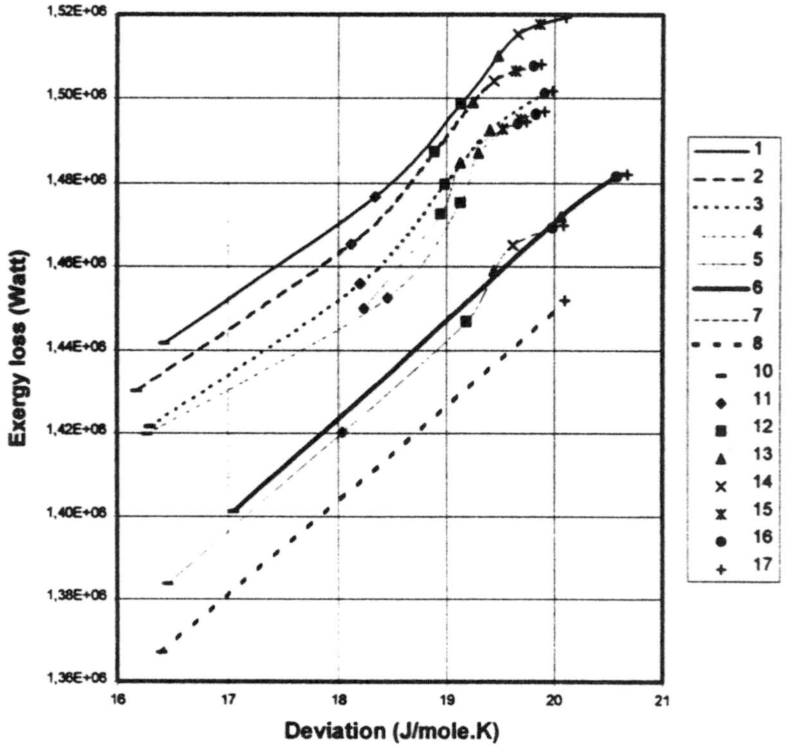

Figure 6.12 : Exergy loss vs. the deviation of the light key (benzene) forces from the optimal course

in the rectifying section on tray 11. This can be seen from in the peak downwards in the stripping section and the peak upwards in the rectifying section at the corresponding trays. It is obvious that the simulated column does not operate according to the principle of equipartition of forces.

As said before, the differences between the points of the 'real' simulation and the equipartitioned points are assumed to be a measure for the excess dissipation on the corresponding trays. It can again be seen from figure 6.10 that the deviations are the largest around the feed, and therefore also the excess dissipation. This is an affirmation that the deviations from the principle could be a measure for the exergy loss. But now the question mentioned in chapter 6.3.5 should be answered: which deviation from which force or combination of forces shows the most correlation with the exergy loss? From the possibilities mentioned before in 6.3.5 and the assumption that only the forces of the light key and the heavy key are important, only the following four sums of deviations are remaining:

1. The sum of the deviations of the light key force (benzene).
2. The sum of the deviations of the heavy key force (toluene).
3. The sum of all the deviations of both forces. So, this is the sum of the first and second possibility.
4. The sum of the deviations of the key force. The light key force is the key force in the stripping section because the stripping section removes primarily the light key. And the heavy key is the key force in the rectifying section because here the heavy key is primarily removed. So, this means that the light key force before the feed and of the heavy key force after the feed is taken as the 'real' force. This possibility also covers the deviation of the force with the largest absolute force from its equipartitioned force.

The results will be presented and discussed in the following subchapter.

6.6.3 The different deviations of the real from the equipartitioned driving forces as a function of the exergy loss

Figure 6.11 gives the sum of the deviations of the real benzene force (the light key component) from the equipartitioned benzene force as a function of the exergy loss for all the combinations of the heat exchanger locations. One line represents a constant location of the heat exchanger in the stripping section and the markers on this line represent the varying position of the heat exchanger in the rectifying section. It is clear that the lines do not show any correlation between the exergy loss and deviation. But the markers on these lines do show some correlation, i.e. the deviation decreases with decreasing exergy loss at constant location of the heat exchanger in the rectifying section. So, it can be concluded that the sum of the deviations of the real light key force from its equipartitioned force shows correlation for exergy loss reduction of the heat exchanger in the stripping section.

The same kind of picture is given in figure 6.12 but now for the sum of the deviations of the real toluene forces (the heavy key component) from the equipartitioned toluene force. So, again the lines are at constant location of the heat exchanger in the stripping section and the markers at constant location of the heat exchanger in the rectifying section. It is obvious that the behaviour has changed drastically. The markers do not

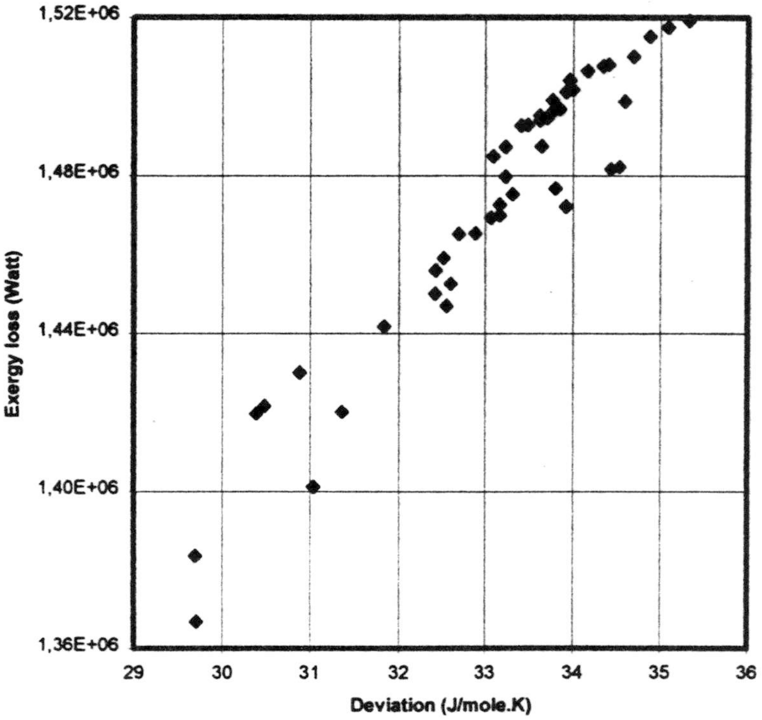

Figure 6.13 : Exergy loss vs. deviation of the sum of the light key forces and heavy key forces from the optimal course

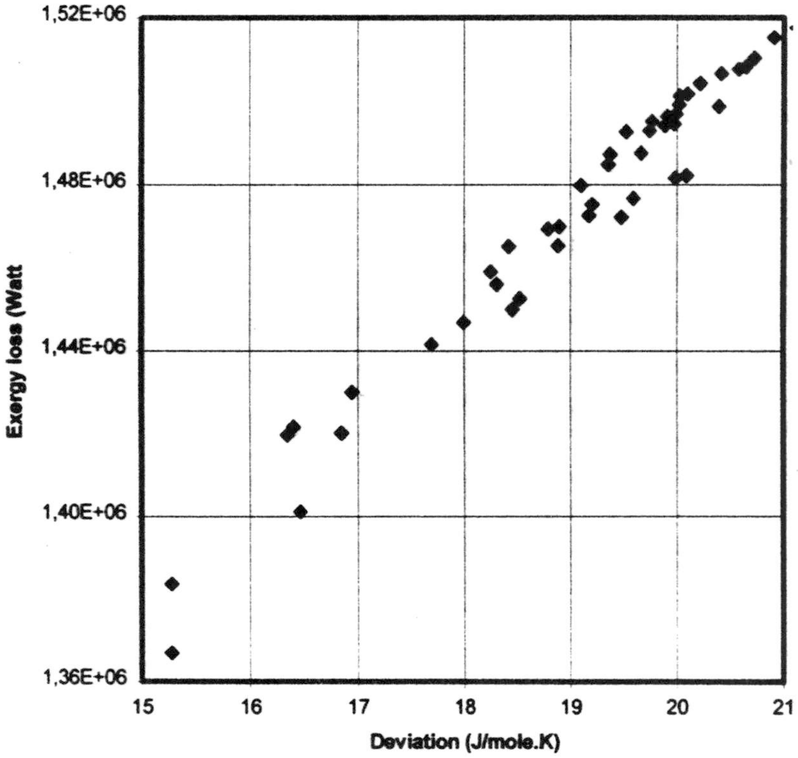

Figure 6.14 : Exergy loss vs. deviation of the key forces from the optimal course

show correlation while the lines do show correlation this time, i.e., the deviation decreases with decreasing exergy loss at constant location of the heat exchanger in the stripping section. So, now the reverse conclusion can be made. The sum of the deviations of the real heavy key force from its equipartitioned force shows correlation for exergy loss reduction of the heat exchanger in the rectifying section.

The following figure 6.13 gives the sum of the deviations of the two previous figures (6.11 and 6.12) as a function of the exergy loss. So, it shows the behaviour of the sum of the deviations of both forces from their equipartitioned forces. It is surprising to see that a linear behaviour is observed. So, the sum of the deviations of the two most important forces is linear with the exergy loss. And therefore the model resulting from the equipartition of forces has usefulness for this type of distillation! No information is given about the position of the heat exchangers because it does not increase the insight of this graph.

As can be seen from figure 6.14, the linear behaviour is improved by taking the sum of the deviations of the light key force in the stripping section and of the heavy key force in the rectifying section from their equipartitioned force, i.e. the key force in each section. This difference in linearity is quantified by calculating the regressions of the two models, which are presented in Table 6.7.

Table 6.7: The regressions of the two models

	Regression
All the deviations	0.901
Deviation from the key force	0.960

Although the regressions are not extremely good, the linear behaviour of the deviations from the ideal model resulting from the equipartition of forces and the exergy loss is justified. And therefore the assumption that only the forces that contribute most to the total entropy production should be taken into account is also justified. So, this simplifies already the application of the principle of equipartition of forces enormously. All the unimportant forces can be left out. But the fact that the deviations from the key force have a larger correlation simplifies the application again. This reduces the number of forces to one: the key force. This can be explained by the assumption that only the contribution of the key force to the total exergy loss is variable and that all the other forces have constant contributions. So, a change in the key force has the largest contribution in the change of the total exergy loss, which is observed in figure 6.14. And this affirms the statement of Sauar[18] that only the force of interest should be equipartitioned and the rest minimised.

The assumption that the transfer area for columns with the same number of heat exchangers is constant is also affirmed. If the transfer areas were not constant the columns with a large transfer area would have the least exergy loss. This can be explained by taking two columns with different transfer area. At constant separation performance the column with a larger transfer area would have a smaller driving force. And a small driving force implies a small exergy loss. The columns where the heat exchangers are placed at the ends of the columns would have the largest transfer area, because the mean liquid and vapour flows are larger. So, these columns should have the least exergy losses and the columns with the heat exchangers around the feed would have the largest exergy losses. As this is not the case the transfer areas can be assumed to be constant.

6.6.4 Distillation as dissipative structure affirmed

Other interesting results from the regression are the intercept and slope of the line presented in figure 6.14. The most interesting is the intercept because this implies that at a deviation of zero still an exergy loss is present. So this means that if a column operates totally ideal in accordance to the principle of equipartition of forces, still an unavoidable exergy loss exists. This is an argument for the statement of De Swaan Arons[2] that a distillation column is a dissipative structure, i.e., one part of the losses is necessary do to the separation and the other part is necessary for the maintenance of the 'structure'.

In order to obtain more insight in this behaviour the calculations are also done for one four other duties of the interstage heat exchangers with constant energy demand. Unfortunately more other duties, which would broaden the range, were not possible because the amount of trays and feed tray position were not constant anymore. So, the assumption of constant transport area in the two sections of the column is not valid anymore and therefore no comparison can be made. The results presented in Table 6.8 are of course based on the most optimal model for the deviations where the sum of the deviations of the key force is taken. Also the exergy loss reduction compared to the column without heat exchangers is given of one pair of locations of the heat exchangers as an example. The location of the heat exchangers is on the 2nd tray in the stripping section and on the 13th in the rectifying section. This choice is based on availability of data and is meant for showing that with increasing duty the reduction increases also. It also shows again that the reduction of the exergy loss is very dependant on the position of the heat exchanger, i.e. the chosen position is not optimal in comparison with Table 6.4.

Table 6.8: The intercepts, slopes exergy loss and exergy loss reduction at different duties of the heat exchangers

Duty (MWatt)	Slope (kmol.K/s)	Intercept (MWatt)	Exergy loss 2-13 (MWatt)	Exergy loss reduction 2-13 (%)
4.0	23.92	0.98	1.485	3.61
3.5	24.04	0.99	1.492	3.16
3.0	23.44	1.02	1.499	2.72
2.5	21.77	1.08	1.506	2.26
2.0	23.07	1.07	1.513	1.81

The values of both slope and intercept differ not enough that a clear conclusion about the dependence of the slope and intercept on the duty can be made. The slope tends to decrease and the intercept tend to increase with decreasing duty. But both statements are not sure and can only be checked with more research. So, only the phenomenon of a slope and an intercept is confirmed again. But more important is that it affirms the assumption that that transfer area is constant at different duties.

Assuming that the intercept is really the unavoidable losses for a specified design of a distillation column, the exergy efficiency of a column can be redefined as:

$$\eta^{redefined} = \frac{\Delta \dot{Ex}_{loss}^{unavoidable}}{\Delta \dot{Ex}_{loss}^{real}} \tag{6.55}$$

While normally thermodynamic efficiency is defined as:

$$\eta^{normal} = \frac{W_{min}}{\Delta \dot{Ex}_{loss}^{real}} \tag{6.56}$$

And the ideal minimum amount of work is defined as:

$$W_{min} = -RT_0\left(\sum_1^i x_i^F \ln x_i^F - \sum_1^i x_i^D \ln x_i^D - \sum_1^i x_i^B \ln x_i^B\right) \tag{6.57}$$

As an example the column used for Table 6.8 is used again. And the average value of the intercept is used for equation (6.55). So, it is assumed that the unavoidable losses do not depend on the duty of the interstage heat exchanger. Table 6.9 gives the results of the two different efficiencies for different duties of the heat exchanger.

Table 6.9: Normal and redefined efficiencies of a column with interstage heat exchangers at the 2nd and 13th tray.

Duty (MWatt)	Efficiency normal	Efficiency redefined
4.0	0.1147	0.6920
3.5	0.1142	0.6888
3.0	0.1136	0.6857
2.5	0.1131	0.6825
2.0	0.1126	0.6794

This redefinition improves the efficiency of distillation remarkably. The reason for these higher redefined efficiencies is of course that the intercept is quite close to the exergy losses of the simulations while the minimum work for separation is only 0.17 MWatt. So, the value of the losses of the most ideal situation is different. The normal efficiency takes the minimum amount of work necessary to perform the separation while the redefined efficiency takes the unavoidable losses. From a very fundamental point of view it is of course correct to take the minimum amount of work as the absolute minimum. But for a more engineering approach, it is more useful to use the redefined efficiency because it really tells how far the design is removed from the most realisable situation. Another advantage of the redefined efficiency is that it is more sensitive to small changes than the normal efficiency. A disadvantage of the redefinition is of course the time costing calculation method.

If this redefined efficiency is taken, the consideration of a distillation column as a dissipative structure is still affirmed but a new part is added. So, the total losses of a column consist now of three parts. The first part is of course the minimum amount of work necessary to perform the separation, which is given by equation (6.57). The

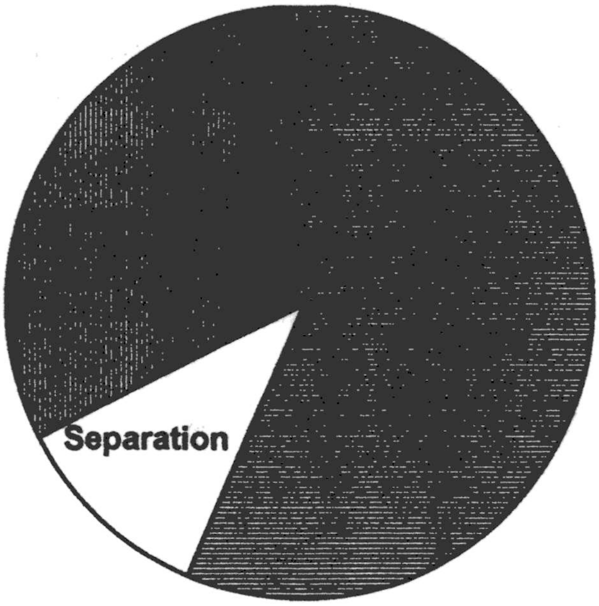

Figure 6.15 : Division of the total losses of a distillation column in three parts

second part is the intercept of the linearity shown in Table 6.8 minus the minimum separation work. This part can be considered as the *minimum* amount of work for maintaining the 'structure'. The rest of the losses which used to be a part of the 'structure' becomes now the excess losses due a non-ideal design of the column. So, for the minimisation of the losses in a column, one should only look at these excess losses because those are the only ones effected by the design.

6.7 Conclusions

The main conclusion for this part of this thesis is that a model based on irreversible thermodynamics is created with several assumptions and that this model is useful for this type of distillation. The usefulness of this model enables the application of the principle of equipartition of forces. This principle of equipartition of forces provides an optimal course of the driving forces. The deviation of the real key driving force from this optimal course is able to describe linearly the exergy loss. And the principle is therefore capable to do what is expected from it beforehand: giving the optimal locations of the heat exchangers. The locations where the key force of a real column deviates most from the equipartitioned key force, are simply the most optimal ones to build in a heat exchanger.

But the most important conclusion is in fact that the principle of equipartition of forces has developed a large step further: a real engineering application is found. So a bridge between irreversible thermodynamics and engineering practice is made. One of the important aspects of the application of the equipartition of forces are the two conditions. The first condition, which states that the total fluxes should be constant, leads at inputs or outputs of mass or energy to other values for the optimal forces. The second condition says that the transport area should be constant and therefore only columns with the same design can be compared. So, only columns with the same number of trays, feed tray and number of interstage heat exchangers can be compared. A very important aspect is the conclusion that only the key force in each part of the column with a constant value for this force is determining for the correlation with the exergy loss. This is a large simplification for the application of the principle of equipartition of forces.

An other striking conclusion is that the deviation of the real key force from the equipartitioned key force has a linear relationship with the exergy loss. This linear relationship has a positive intercept and this means that an unavoidable exergy loss is present in the most ideal situation, i.e. the forces are totally equipartitioned according to the principle of equipartition of forces. In other words all the optimisation methods should only look at the avoidable part, which can be deduced from the principle. This is an other affirmation for considering distillation as a dissipative structure. But this intercept from has a much larger value than the unavoidable losses due to only separation. So, the unavoidable losses contain also a part due to the maintenance of the structure. Therefore the efficiency of distillation can be increased in if this intercept is used as the unavoidable losses and not the minimum amount of work necessary for the separation.

7. Conclusions and recommendations

7.1 Conclusions

7.1.1 Main conclusion

The aim of this final thesis is successfully pursued. An application and comparison of several thermodynamic analysis methods for the sequencing of columns, the feed tray location and the location of interstage heat exchangers in multi component distillation are achieved.

7.1.2 Conclusions from previous chapters

The conclusions already made at the end of each chapter are repeated here shortly:

1. The program written in the programming language C and based on the tray-to-tray calculation method gives accurate simulations of various kinds of columns and types of mixtures.
2. A new and very fast method of calculating equilibria based on the combination of a calculated grid and an interpolation technique is successfully developed. So, the time consuming equilibrium calculations with an equation of state and/or model for activity coefficients have only to be done once.
3. The maximum number of components that can be analysed with this program, is limited to three due to memory limitations of the software.
4. The sum of the exergy losses due to heat exchange of the separate columns in a sequence is able to predict the optimal sequence of those columns well enough to give a large reduction in the number of possibilities of sequencing.
5. It is surprising that the exergy loss calculated with more assumptions predicts the optimal sequence better than that with fewer assumptions.
6. The already in literature available method of using the total vapour load for the sequencing has proved to be worse than both exergy loss based methods.
7. The entropy production rate due to mixing on the feed tray predicts the optimal feed tray better than the exergy loss due to the same mixing, but should be equivalent. However, this conclusion could be very dependant on how the mixing and the thermodynamic model are defined.
8. The temperature difference of the two flows which are mixed has a far worse predictive power for the optimal feed tray location than the entropy production and exergy loss due to mixing on the feed tray.
9. An application is found for the principle of equipartition of forces and therefore the principle has been developed further. The proof for this application is the correlation between the exergy loss and the deviation of the simulated results from the equipartitioned course of the key force.
10. The principle of equipartition of forces is able to predict the optimal locations for interstage heat exchangers.
11. The consideration of a distillation column as a dissipative structure is affirmed by the application of the principle of equipartition of forces.

7.1.3 **Overall conclusions**

The first overall conclusion is that exergy analysis has proved to be a very good thermodynamic analysis tool for distillation. It was able to give the optimal sequence and the optimal locations of the interstage heat exchangers. The performance of exergy was not very good for the feed tray but perhaps a better definition of the mixing and thermodynamic model could improve this. This is as a whole in fact a surprising result because a lot of research has been done on distillation the last decades. So, it could be expected more likely that not much new results would be obtained because already everything is found out. But exergy analysis has proved that it can be very useful even in topics that are very well known and often analysed. So, a lot more successful analyses can be expected from exergy analysis.

As already mentioned, the application of the principle of equipartition of forces has lead to the further development of this principle. Due to this further development, a new thermodynamic tool has stepped out of its infancy and has very promising qualities. It is able to locate losses. This is not new because exergy analysis is also able to do this. But it is also able to quantify the variables that should be changed in order to come to the optimal design. Exergy loss is not able to do this because it is a general model and is caused by the sum of contributions of all driving forces, i.e. it provides no model for the optimal design. So, in principle the equipartition of forces is more powerful than exergy analysis but it will always need the backup of an exergy analysis because the equations for the forces are always based on several assumptions about the transfer rate. And in order to know if these assumptions are correct and interwoven, an exergy analysis is always necessary.

7.2 **Recommendations**

The main recommendation is to develop the principle of equipartition further so it can become a real engineering tool with which losses and the related variables can be locate, quantified and finally diminished. For this aim, first of all the equipartition should be mathematically proved in all its aspects. This implies not only the principle itself but also all the necessary derivations of all the forces with their possible mechanisms and assumptions present in process design. And also a lot of applications should be pursued, which will automatically lead to more insight. Chemical reactors and separation methods other than distillation are very interesting further applications.

For the analysis of distillation columns with the equipartition of forces it would also be useful to do an analysis of the temperature forces. This analysis was left out in this thesis because only the largely contributing forces were assumed to be important. But the temperature force could also give very interesting information because the phenomenon of distillation is a based on temperature difference.

The last recommendation resulting from the equipartition is to analyse the consideration of a distillation column as a dissipative structure further. Perhaps it is possible to make a more generally valid distinction between the avoidable and unavoidable losses in which all the distillation parameters are considered. This would be very useful to know because then optimisations will know their limits in each design.

This thesis could also be a basis for the investigation of the flexibility and maximum output of a distillation column. In this thesis is already found that a reflux ratio exists where the column has a maximum flexibility with respect to the number of possible feed tray locations. This flexibility and maximum output are very important parameters for modern distillation because the economical markets vary always. And it would be very useful to know what the upper and lower performance limits are of a distillation column and how the variables should be set in order to obtain the least losses at these limits. So, on every change in the market could then be optimally anticipated by increasing or decreasing the performance of the column with the least increase in losses.

For the feed tray analyses it is not only recommended to improve the definition of the thermodynamic model and mixing on the feed tray; so the suspicions about the thermodynamic model and possible contribution of evaporation and condensation can be analysed. But also other mechanisms and criteria should be analysed. The analysis done in this thesis shows that the mixing shows a lot correlation with the optimal feed tray location. But perhaps other variables related to other mechanisms will show more correlation.

8. Symbols

B	Bottom flow	mole/s
D	Distillate flow	mole/s
E	Energy	J
Ex	Exergy	J
F	Feed	mole/s
g	Gravity constant (= 9.81)	m/s^2
G	Gibbs energy	J
H	Enthalpy	J
J	Flux	mole/s
L	Liquid flow	mole/s
L_{kl}	Transport coefficient	various
n	Tray number	-
N	Number of trays	-
m	Mass flow	mole/s
P	Pressure	bar/mmHg
$P^{B/D}$	Recovery	-
q	See equation (3.45)	-
Q	Heat	J
r	Fraction vapour in feed	-
R	Reflux ratio	-
R^{gas}	Gas constant	J/mole.K
S	Entropy	J/K
t	Time	s
T	Temperature	K
u	Speed	m/s
V	Vapour flow	mole/s
W	Work	J
x	Liquid mole fraction	-
X	Force	various
y	Vapour mole fraction	-
z	Height	m

Greek

α	Relative volatility	-
μ	Chemical Potential	J/mole
Θ	Constant used in Underwood equations	-
ψ	Ratio between actual reflux ratio and minimum reflux ratio	-

Sub/superscripts

0	Environmental conditions (T=298.15 , P=1.0 bar)
Act	Actual
Ant	Antoine's

av	Average
B	Bottom
boil	Boiling
comp	Components
cond	Condenser
D	Distillate
driv	Driving
est	Estimation
F	Feed
Ftray	Feed tray number
h	Component number
HK	Heavy key
HnK	Heavy non-key
HX	Heat exchanger
i	Component number
id	Ideal dilution
ig	Ideal gas
init	Initial
irr	Irreversible
j	Total number of columns
k	Total number of forces
l	Total number of forces
liq	Liquid
LH	Light key - Heavy key
LK	Light key
LnK	Light non-key
m	Total number of components
min	Minimum
mix	Mixing
n	Tray number
N	Total number of trays
q	Heat
reb	Reboiler
rect	Rectifying section
res	Reservoir
rev	Reversible
S	Shaft
strip	Stripping section
T	Constant temperature
vap	Vapour / Vaporisation

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10. Appendices

10.1 Example of Underwood calculations.

This example is taken from Coulson&Richardson [1, page 424].

First of all a summary of data necessary for the calculation is given for this example in Table 10.1.

Table 10.1 : The data for the example

	α	Feed (mole/s)	Distillate (mole/s)	Bottom (mole/s)
C_3	5	5	5	0
iC_4	2.6	15	14.9	0.1
nC_4 (LK)	2.0	25	24	1
iC_5 (HK)	1	20	1	19
nC_5	0.85	35	0.4	34.6
Total		100	45.3	54.7

Note that the relative volatilities are taken relative to one component in the row and not like in the sequencing analysis where the relative volatilities are taken relative to consecutive pairs of components.

As the feed is totally liquid the q in equation (3.42) becomes 0.

So:

$$\sum \frac{\alpha_i x_i^F}{\alpha_i - \theta} = 0 \qquad (10.1)$$

An iteration procedure is used in order to obtain the value of θ. The results of such an iteration procedure are presented in Table 10.2.

Table 10.2 : The iteration of Θ

x_i^F	α_i	$\alpha_i x_i^F$	$\theta=1.5$	$\theta=1.3$	$\theta=1.35$
0.05	5	0.25	0.071	0.068	0.068
0.15	2.6	0.39	0.355	0.300	0.312
0.25	2.0	0.50	1.000	0.714	0.769
0.20	1	1	-0.400	-0.667	-0.571
0.35	0.85	0.85	-0.462	-0.667	-0.600
			$\sum$=0.564	-0.252	0.022 close enough

This value for Θ is substituted in equation (10.1). The results are shown in Table 10.3

Table 10.3 : Calculation of the minimum reflux ratio

x_i^D	α_i	$\alpha_i x_i^D$	$\frac{\alpha_i x_i^D}{\alpha_i - \theta}$
0.11	5	0.55	0.15
0.33	2.6	0.86	0.69
0.53	2.0	1.08	1.66
0.02	1	0.02	-0.06
0.01	0.85	0.01	0.02
			$\sum = 2.42$

So:

$R_{\min} + 1 = 2.42$

$R_{\min} = 1.42$

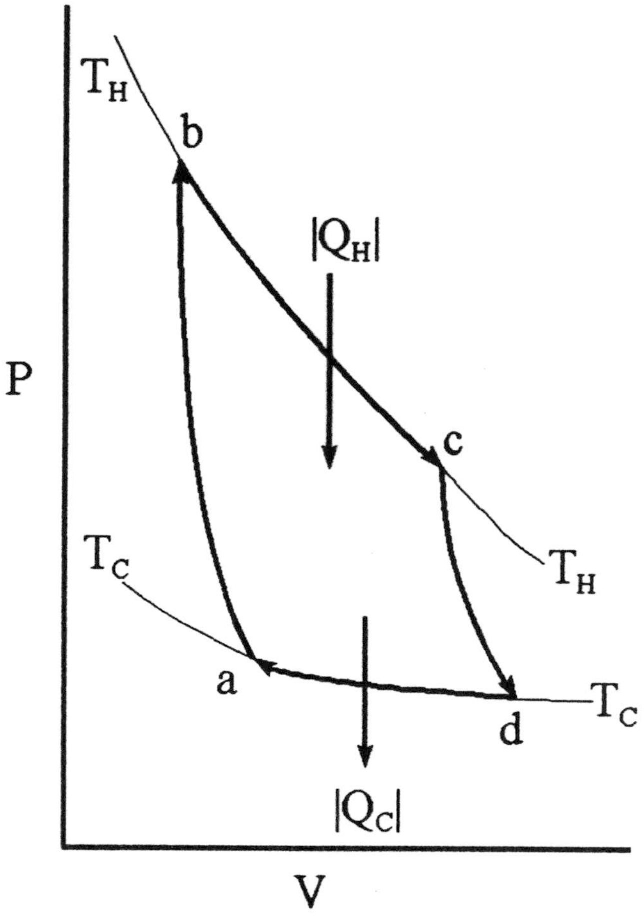

Figure 10.1 : Pressure-Volume diagram for a Carnot cycle

10.2 Derivation of the efficiency of the Carnot cycle.

This part is based on Smith&Van Ness [19, page 140-147].

The Carnot cycle consists of the next four elements:

1. a→b Adiabatic compression from T_C until the temperature rises to T_H.
2. b→c Isothermal expansion to arbitrary point c with absorption of $|Q_H|$.
3. c→d Adiabatic expansion until the temperature decreases to T_C.
4. d→a Isothermal compression to the initial state with rejection of heat $|Q_C|$.

Figure 10.1 represents this cycle in a P-V diagram.

The first law for this cycle states that the work produced by $|Q_H|$ is expressed as:

$$W = Q = |Q_H| - |Q_C| \qquad (10.2)$$

So, the thermal efficiency can be defined as:

$$\eta = \frac{W}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|} \qquad (10.3)$$

In order to obtain this efficiency in manageable terms, the ratio between $|Q_H|$ and $|Q_C|$ is rewritten with the following derivation

The first law for reversible processes with an ideal gas is given by:

$$dQ = C_V dT + PdV \qquad (10.4)$$

Now $|Q_H|$ is given as:

$$|Q_H| = \int_{V_b}^{V_c} PdV = RT_H \ln\frac{V_C}{V_b} \qquad (10.5)$$

Similarly for the isothermal step d→a:

$$Q_{da} = RT_C \ln\frac{V_d}{V_a} \qquad (10.6)$$

Now the $|Q_c|$ becomes:

$$|Q_C| = RT_C \ln\frac{V_d}{V_a} \qquad (10.7)$$

The ratio is rewritten:

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C}\frac{\ln(V_c / V_b)}{\ln(V_d / V_a)} \qquad (10.8)$$

For an adiabatic process equation (10.8) can be rewritten:

$$-C_V dT = PdV = \frac{RT}{V} dV \tag{10.9}$$

or:

$$-\frac{C_V}{R}\frac{dT}{T} = \frac{dV}{V} \tag{10.10}$$

For step a→b:, integration gives:

$$\int_{T_C}^{T_H} \frac{C_V}{R}\frac{dT}{T} = \ln\frac{V_a}{V_b} \tag{10.11}$$

Similarly, for step c→d:

$$\int_{T_H}^{T_C} \frac{C_V}{R}\frac{dT}{T} = -\ln\frac{V_d}{V_c} \tag{10.12}$$

Since the left-handed sides of these two equations are the same:

$$\ln\frac{V_a}{V_b} = \ln\frac{V_d}{V_c} \tag{10.13}$$

This may also be written:

$$\ln\frac{V_c}{V_b} = \ln\frac{V_d}{V_a} \tag{10.14}$$

With the final result:

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C} \tag{10.15}$$

and:

$$\eta = 1 - \frac{T_C}{T_H} \tag{10.16}$$

10.3 The enthalpies of vaporisation and boiling temperatures

Table 10.4: The enthalpies of vaporisation at 298.15 K

	Mixture 1		Mixture 2		Mixture 3	
	Component	$\Delta_{vap}H$ (J/mole)	Component	$\Delta_{vap}H$ (J/mole)	Component	$\Delta_{vap}H$ (J/mole)
A	n-pentane	25790	Propane	19040	Ethanol	38560
B	n-hexane	28850	i-butane	21300	i-propanol	39850
C	n-heptane	31770	n-butane	22440	n-propanol	41440
D	n-octane	34310	i-pentane	24690	i-butanol	41820
E	n-decane	38750	n-pentane	25790	n-butanol	43290

Table 10.5: The boiling temperatures at atmospheric pressure

	Mixture 1		Mixture 2		Mixture 3	
	Component	T_{boil} (K)	Component	T_{boil} (K)	Component	T_{boil} (K)
A	n-pentane	309.21	Propane	231.05	Ethanol	351.44
B	n-hexane	341.88	i-butane	261.42	i-propanol	356.45
C	n-heptane	371.65	n-butane	272.65	n-propanol	370.35
D	n-octane	398.82	i-pentane	301.03	i-butanol	381.04
E	n-decane	447.3	n-pentane	309.21	n-butanol	390.88

10.4 The Antoine's constants

Table 10.6 : The Antoine's constants for the sequencing

	A^{Ant}	B^{Ant}	C^{Ant}
n-pentane	6.85221	1064.63	232
n-hexane	6.87776	1171.53	224.366
n-heptane	6.9024	1268.115	216.9
n-octane	6.92377	1355.126	209.517
n-decane	6.95367	1501.268	194.48
Propane	6.82973	813.2	248
I-butane	6.74808	882.8	240
n-butane	6.83029	945.9	240
I-pentane	6.78979	1020.01	233.09
Ethanol	8.1122	1592.864	226.184
I-propanol	8.87829	2010.33	252.636
n-propanol	8.37895	1788.02	227.438
I-butanol	8.53616	1950.94	237.147
n-butanol	7.83029	1558.19	196.881

The Antoine's equation is given by:

$$\log P^{sat} = A^{Ant} - \frac{B^{Ant}}{T + C^{Ant}} \tag{10.17}$$

And the relative volatility:

$$\alpha_{12} = \frac{P_1^{sat}}{P_2^{sat}} \tag{10.18}$$

For the temperature (in °C), at which the relative volatility of two components is calculated, is chosen for the average boiling temperature of the two components at atmospheric pressure. The pressure is given in mmHg.

10.5 The data for the evaluation of the sequencing

Table 10.7: Results for mixture 1

	Ideal exergy loss(J/mole)	Vapour load	Non-ideal exergy loss(J/mole)	TAC($/y)	Annual equipment cost($/y)	Annual steam cost($/y)	Annual brine cost($/y)
1	7002.60	2.2152	12803.49	1993666	738866	716300	538500
2	8933.26	2.4529	13401.06	2172730	800630	776500	595600
3	7325.91	2.3497	13278.96	2024653	769053	716700	538900
4	10153.74	2.5915	19303.65	2295003	844203	817000	633800
5	10696.16	2.8034	15691.15	2342195	862395	831900	647900
6	8621.73	2.3399	13201.63	2126172	803372	751200	571600
7	6691.08	2.1022	12604.06	1947128	741628	691000	514500
8	7437.65	2.4027	14458.02	2127581	798981	754200	574400
9	7640.31	2.4730	15851.31	2119849	807249	746000	566600
10	12090.26	3.0888	19238.07	2560200	991600	875200	693400
11	11887.60	3.0185	18697.31	2567812	983312	883400	701100
12	10921.91	2.6406	16349.11	2364307	923507	809600	631200
13	11555.50	2.8869	17226.23	2468332	932432	858400	677500
14	11013.08	2.6750	16146.64	2445989	996986	813600	635403

Table 10.8: Results for mixture 2

	Ideal exergy loss(J/mole)	Vapour load	Non-ideal exergy loss(J/mole)	TAC($/y)	Annual equipment cost($/y)	Annual steam cost($/y)	Annual brine cost($/y)
1	7676.68	7.9652	14121.28	4096404	1713604	1253700	1129100
2	7826.63	9.0402	23293.26	4063666	1763966	1210900	1088800
3	6961.93	6.3998	11152.30	4001969	1705169	1209400	1087400
4	7449.92	8.6836	26428.50	4012243	1751543	1190800	1069900
5	7559.94	8.2848	25242.71	4023955	1755455	1194800	1073700
6	6467.72	8.3769	23384.86	3891783	1719083	1145500	1027200
7	6317.77	7.3019	14212.89	3925767	1668967	1188800	1068000
8	6116.15	5.8840	10996.51	3929901	1682201	1184100	1063600
9	5796.80	5.8257	12628.35	3861248	1665148	1157500	1038600
10	6544.16	7.9807	28236.47	3872658	1719558	1135400	1017700
11	6863.51	8.0390	27644.28	3941161	1736561	1161900	1042700
12	6240.37	8.2902	28655.13	3847703	1712003	1126400	1009300
13	7047.76	8.1698	27487.63	3974328	1753428	1170300	1050600
14	6937.74	8.5686	28260.49	3874399	1674699	1159400	1040300

Table 10.9: Results for mixture 3

	Ideal exergy loss(J/mole)	Vapour load	Non-ideal exergy loss(J/mole)	TAC($/y)	Annual equipment cost($/y)	Annual steam cost($/y)	Annual brine cost($/y)
1	6474.39	10.1015	13241.50	5799690	1890090	2052500	1857100
2	7516.89	10.4564	13901.72	6088422	1934222	2178100	1976100
3	6325.28	8.0176	13450.77	5883374	1892874	2094000	1896500
4	7712.02	9.2226	16080.13	6167327	1962327	2272400	1932600
5	7950.97	8.6388	15048.35	6289209	1951409	2272400	2065400
6	7368.10	12.9105	10130.02	6034425	1846525	2195400	1992500
7	6325.59	12.5555	9469.81	5745693	1802393	2069800	1873500
8	6796.27	8.5878	13911.79	6277053	2107153	2186200	1983700
9	7005.91	11.1652	13196.79	6316510	2033610	2244200	2038700
10	9603.57	12.2300	17418.18	6931475	2134975	2508000	2288500
11	9393.94	9.6527	19379.18	6892077	2208577	2450000	2233500
12	8535.21	12.1203	14966.03	6381971	1932371	2329800	2119800
13	8707.89	9.0084	18285.79	6472963	1992263	2345800	2134900
14	8468.94	9.5923	17527.24	6242953	1944053	2252400	2046500

10.6 The data of the feed tray analyses

Table 10.10 : Data of the feed of 0.3/0.35/0.35

Reflux ratio	Ftray	$x^D_{benzene}$	ΔT(K)	Ex_{mix} (J/s)	ΔS_{mix} (J/s.K)
2.892	11	0.999119	6.19	37255	93
	12	0.999117	11.12	53763	92
4.338	9	0.999027	3.21	57164	174
	10	0.999173	9.32	64521	144
	11	0.999098	14.13	87547	136
5.785	9	0.999057	7.25	71748	186
	10	0.999091	13.18	103602	200
	11	0.999011	17.32	157478	275
7.231	8	0.999341	2.99	75981	233
	9	0.999391	9.46	82059	194
	10	0.999382	14.91	116388	199
	11	0.99929	18.58	186036	320
	12	0.99911	20.45	224840	386
8.677	7	0.999377	-1.14	99602	322
	8	0.999526	4.96	111772	337
	9	0.999544	11.34	121469	290
	10	0.999517	16.31	170821	333
	11	0.999448	19.41	214184	380
	12	0.999296	21.03	261831	479
10.123	8	0.999095	5.7	93787	273
	9	0.999117	12.07	117126	256
	10	0.999056	17	173448	318

Table 10.11 : Data of the feed of 0.5/0.25/0.25

Reflux ratio	Ftray	$x^D_{benzene}$	$\Delta T(K)$	Ex_{mix} (J/s)	ΔS_{mix} (J/s.K)
4.972	11	0.999206	6.04	32800	86
	12	0.999209	9.36	53120	109
7.458	9	0.999366	-0.05	69500	242
	10	0.999497	6.02	68355	201
	11	0.999519	9.76	71946	157
	12	0.999444	11.82	94693	190
	13	0.999192	12.84	152740	237
9.944	8	0.999106	-4.3	83186	282
	9	0.999347	2.69	54845	184
	10	0.999404	8.05	69286	175
	11	0.999364	11.23	107436	238
	12	0.999264	12.86	140251	310
11.187	8	0.999274	3.41	103477	347.1
	9	0.999446	3.51	77291	254.1
	10	0.999468	8.49	84984	218.7
	11	0.999448	11.55	122956	284.5
	12	0.999344	13	149121	334.6
	13	0.999060	13.72	163886	364.6
12.430	8	0.999431	-2.53	102671	353
	9	0.999544	4.03	78546	251
	10	0.999564	9.07	100133	256
	11	0.999523	11.78	126696	284
	12	0.999428	13.11	153544	354
	13	0.999197	13.83	186177	433
14.916	9	0.999084	5.07	106866	337.4
	10	0.999122	9.62	109851	276.6
	11	0.999077	12.24	140039	319.2

Table 10.12 : Data of the feed 0.7/0.15/0.15

Reflux ratio	Ftray	$x^D_{benzene}$	ΔT(K)	Ex_{mix} (J/s)	ΔS_{mix} (J/s.K)
9.924	11	0.999152	3.67	30089	97
	12	0.999157	5.6	41206	115
14.887	9	0.999049	-3.04	70077	251
	10	0.999244	2.13	41320	148
	11	0.999326	5.05	43807	128
	12	0.999271	6.47	49410	129
	13	0.999019	7.05	81824	228
17.368	9	0.999364	-2.25	59540	218.9
	10	0.999472	2.75	47174	161.3
	11	0.999481	5.49	48088	138.1
	12	0.999437	6.62	48818	123.6
	13	0.999268	7.21	64128	166.4
19.849	8	0.999285	-8.53	111891	346
	9	0.999498	-1.37	73757	266
	10	0.999541	3.21	43020	146
	11	0.999563	5.68	63406	184
	12	0.99954	6.76	77573	216
	13	0.999396	7.4	84543	229
	14	0.999047	7.51	96460	268
24.811	9	0.999062	-0.76	44745	171
	10	0.999206	3.65	39467	128
	11	0.9992	5.93	64706	182
	12	0.999108	7.09	83425	231

Table 10.13: The regressions of the feed tray analyses

Benzene feed mole fraction	Reflux ratio	Temperature difference	Exergy loss	Entropy production rate	Number of points
0.3	4.338	0.297	0.047	0.544	3
	5.785	0.236	0.472	0.696	3
	7.231	0.328	0.631	0.910	5
	8.677	0.055	0.322	0.621	6
	10.123	0.328	0.631	0.991	3
0.5	7.458	0.040	0.748	0.625	5
	9.944	0.059	0.039	0.521	7
	11.187	0.132	0.529	0.715	6
	12.430	0.198	0.719	0.929	6
	14.196	$8.3\ 10^{-5}$	0.307	0.818	3
0.7	14.887	0.009	0.897	0.936	5
	17.368	0.099	0.949	0.216	5
	19.849	0.302	0.526	0.376	7
	24.811	0.165	0.020	0.220	4
mean		0.165	0.497	0.651	
standard deviation		0.129	0.312	0.257	

10.7 Fluxes and forces

This appendix gives the data and results of the method of calculation of the fluxes and forces used for the comparison of a column with heat exchangers and without heat exchangers as described in chapter 6.5.

First of all the values of the main results as presented in the figures 6.6, 6.7 and 6.7 are presented in Table 10.14.

Table 10.14: Data of the exergy losses per tray and the comparison of the UNIQUAC-Redlich-Kwong and the irreversible thermodynamics results

	Entropy production rate (J/s.K)				Exergy loss (J/s)	
Tray no.	with heat exchangers		without heat exchangers		with heat exchangers	without exchangers
	UNIQ-RK	irreversible	UNIQ-RK	irreversible		
1	579,0903		715,4433		172655,8	213309,4
2	191,1479	228,52744	247,8599	298,05041	56990,76	73899,42
3	88,512	108,30409	123,8657	139,14335	26389,85	36930,58
4	45,21823	61,532224	75,5388	92,06556	13481,82	22521,89
5	35,21698	59,841274	46,08066	61,44224	10499,94	13738,95
6	56,45299	62,361263	53,80938	75,466347	16831,45	16043,25
7	101,1549	111,73906	181,888	156,31622	30159,36	54229,92
8	210,9672	191,00162	281,2406	266,10719	62899,86	83851,9
9	555,3824	534,83542	447,6626	419,9794	165587,3	133470,6
10	538,87	557,87374	529,4704	553,41957	160664,1	157861,6
11	998,2491	934,07872	790,7879	544,73072	266655,1	236195,3
12	242,6285	340,50324	437,5143	434,65331	103734,5	130444,9
13	204,6513	193,8847	283,066	295,90033	61016,8	84396,14
14	106,724	103,20362	160,7334	154,50767	31819,76	47922,68
15	43,29908	53,94726	67,36882	77,297051	12909,62	20086,01
16	30,13821	26,097582	40,56406	36,19408	8985,707	12094,17
17	14,31557	12,469262	18,80159	16,805238	4268,189	5605,696
18	6,795397	6,1020037	8,707827	7,9661112	2026,045	2596,239
19	534,3022		656,5339		159397,8	195842,6

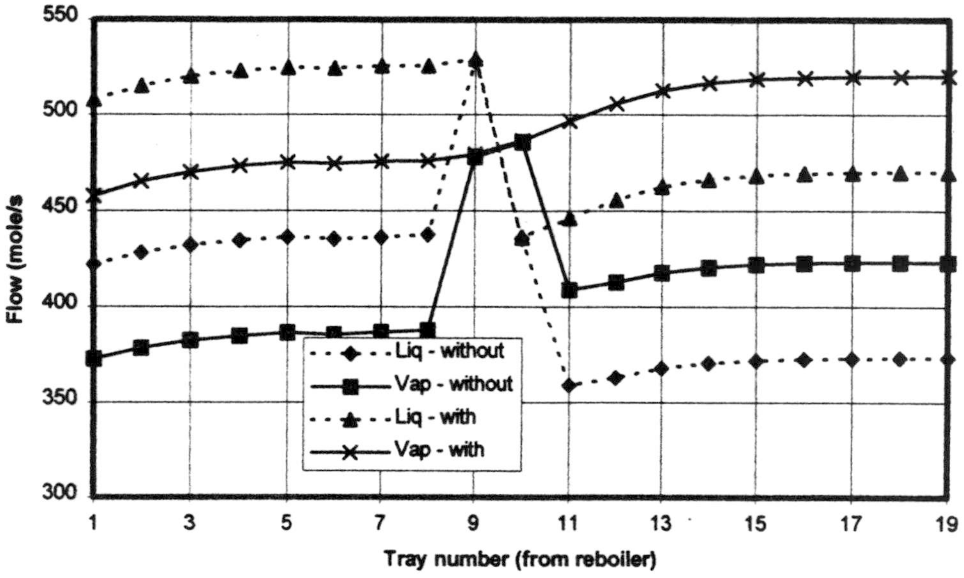

Figure 10.2 : Liquid and vapour flows in the column with heat exchangers and in the column without heat exchangers

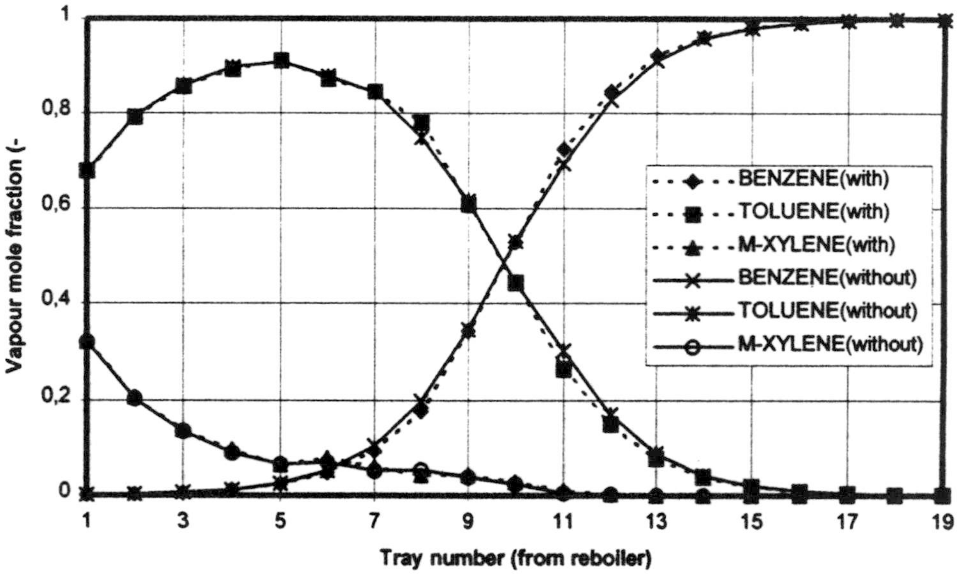

Figure 10.3 : Vapour mole fractions in the column with heat exchangers and in the column without heat exchangers

The first necessary variables which should be known are the vapour and liquid flows in the columns. These are give in Table 10.15 and figure 10.2.

Table 10.15 :The liquid and vapour flows in the columns with and without heat exchangers

Tray	with heat exchangers		without heat exchangers	
	Liquid flow (mole/s)	Vapour flow (mole/s)	Liquid flow (mole/s)	Vapour flow (mole/s)
1	422,4719	372,5221	507,6302	457,6804
2	428,4375	378,4876	515,1558	465,2059
3	432,2176	382,2678	519,887	469,9372
4	434,6201	384,6702	523,1335	473,1836
5	436,4364	386,4866	524,8222	474,8723
6	435,421	385,4711	524,3574	474,4075
7	436,4737	386,5239	525,6154	475,6656
8	437,7634	387,8136	525,7901	475,8403
9	528,1041	478,1542	529,2065	479,2567
10	435,594	485,6441	436,203	486,2532
11	358,8966	408,9467	446,4599	496,51
12	362,8645	412,9146	455,6434	505,6936
13	368,0177	418,0679	462,603	512,6531
14	370,7117	420,7618	466,4956	516,5457
15	372,137	422,1872	468,4642	518,5143
16	372,8321	422,8822	469,3996	519,4498
17	373,1622	423,2124	469,8332	519,8834
18	373,3189	423,3691	470,0341	520,0842
19	373,393	423,4432	470,1268	520,1769

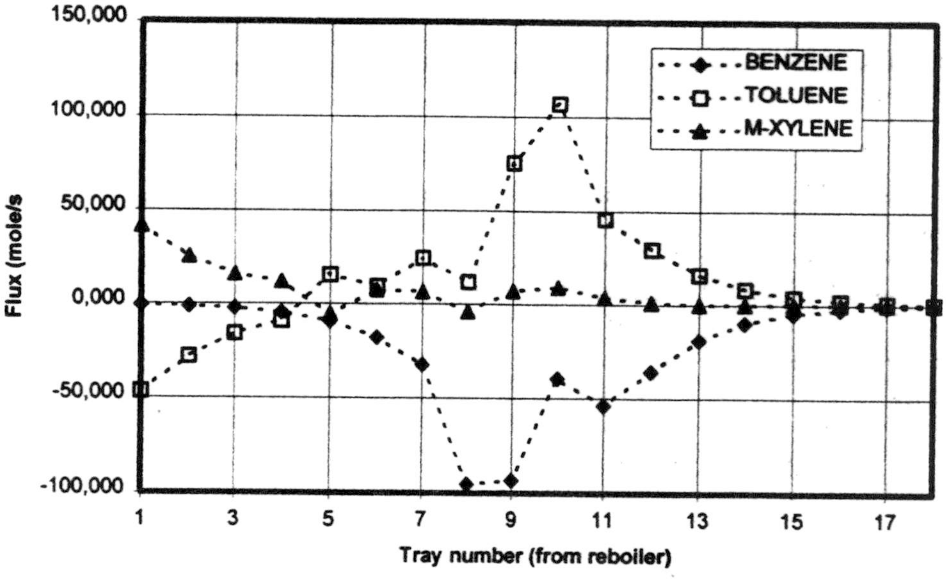

Figure 10.4 : Mass fluxes in the column with heat exchangers

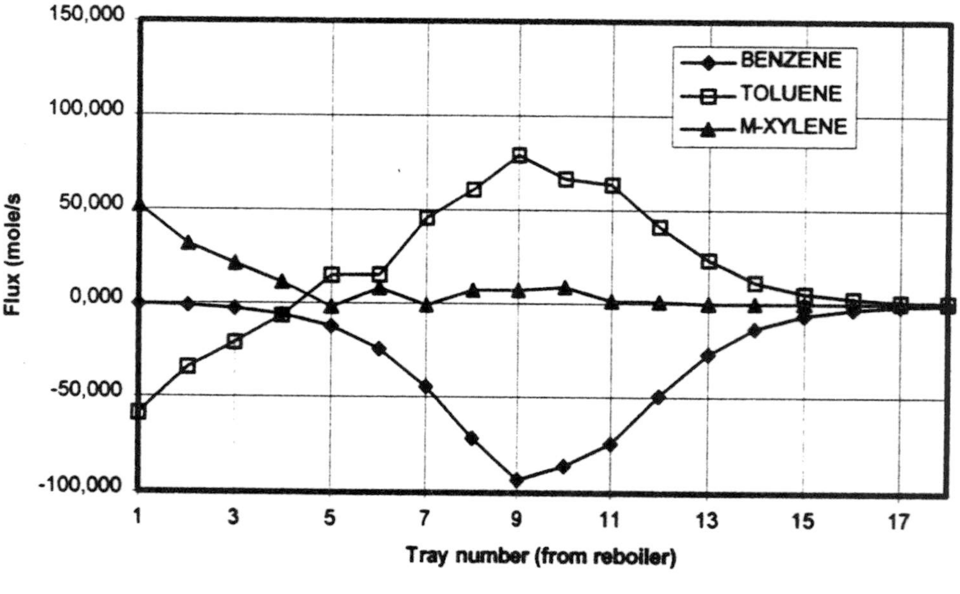

Figure 10.5 : Mass fluxes in the column without heat exchangers

The second values necessary for the calculations of the fluxes are the mole fractions in the vapour. Table 10.16 and figure 10.3 gives them.

Table 10.16: The vapour mole fractions per tray for the columns with and without heat exchangers

Tray	with			without		
	$y_{benzene}$	$y_{toluene}$	$y_{m\text{-}xylene}$	$y_{benzene}$	$y_{toluene}$	$y_{m\text{-}xylene}$
1	0,0012789	0,6783282	0,3203929	0,0012789	0,6783282	0,3203929
2	0,0028373	0,791227	0,2059357	0,0028742	0,7936222	0,2035035
3	0,0059455	0,8563218	0,1377327	0,0060728	0,8590217	0,1349055
4	0,0120044	0,8922441	0,0957515	0,012607	0,8979821	0,089411
5	0,0239293	0,91165	0,0644207	0,0256513	0,9089812	0,0653675
6	0,0475973	0,8734241	0,0789787	0,0520992	0,8785102	0,0693906
7	0,0936365	0,8464918	0,0598717	0,1039781	0,8441478	0,0518742
8	0,1767746	0,7803799	0,0428455	0,1979498	0,7481883	0,0538619
9	0,3426508	0,6078656	0,0430663	0,3453156	0,6160398	0,0386447
10	0,5289423	0,4429273	0,0281305	0,5318802	0,444552	0,0235679
11	0,724703	0,2642259	0,0110712	0,6934714	0,3011884	0,0053402
12	0,8476364	0,150211	0,0021526	0,8273065	0,1702755	0,002418
13	0,9225948	0,0774052	0	0,9120658	0,0877086	0,0002256
14	0,9617275	0,0382725	0	0,9578325	0,0421582	9,277E-06
15	0,9817604	0,0182396	0	0,9804077	0,0195923	0
16	0,9914149	0,0085851	0	0,9909887	0,0090113	0
17	0,9959896	0,0040104	0	0,9958802	0,0041198	0
18	0,9981587	0,0018413	0	0,9981429	0,0018571	0
19	0,999184	0,000816	0	0,9991867	0,0008133	0

Now the fluxes can be calculated with equation (6.23) and (6.25) and the table 10.17 and figures 10.4, 10.5 and 10.6 give the results. The thermal fluxes vary a lot, even from negative to positive. In principle this is not possible, they should be according to the definition always negative. So, the assumptions made for equation (6.25) are not correct.

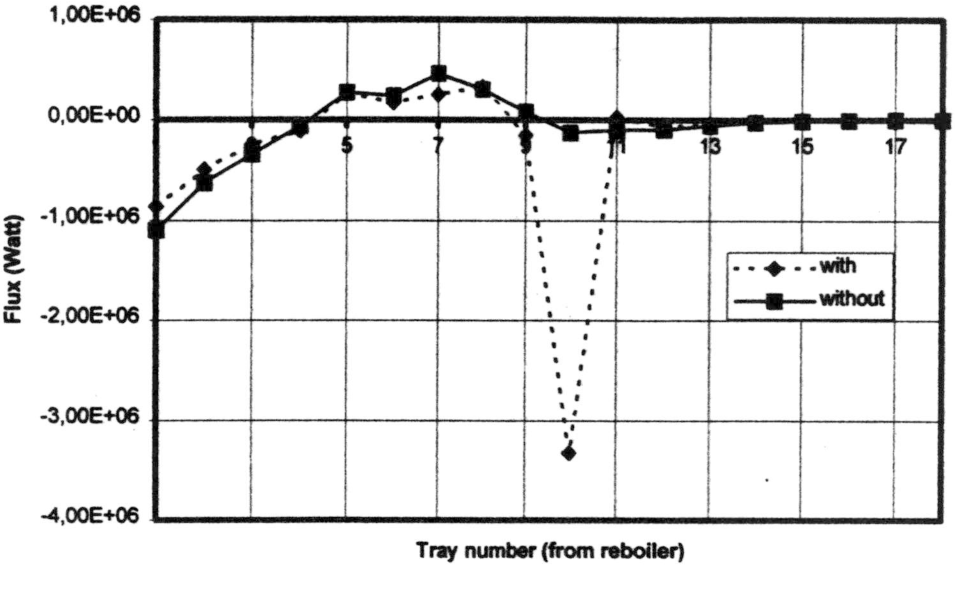

Figure 10.6 : Thermal fluxes in the column with heat exchangers and in the column without heat exchangers

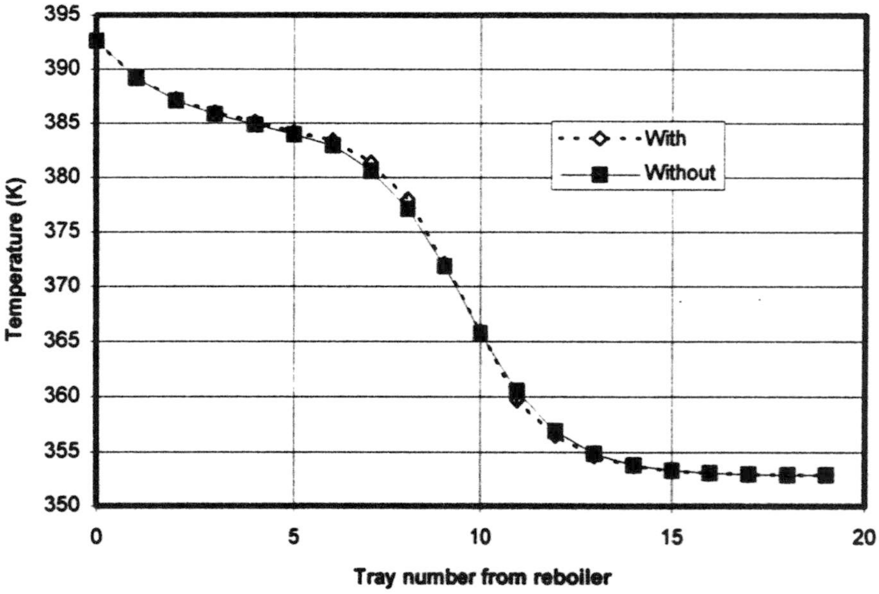

Figure 10.7 Temperatures of the liquid flows in the column with heat exchangers and in the column without heat exchangers

Table 10.17: The mass and thermal fluxes per tray for the columns with and without heat exchangers

Tray	With heat exchangers				without heat exchangers			
	$J_{benzene}$ (mole/s)	$J_{toluene}$ (mole/s)	$J_{m\text{-}xylene}$ (mole/s)	J'_q (J/s)	$J_{benzene}$ (mole/s)	$J_{toluene}$ (mole/s)	$J_{m\text{-}xylene}$ (mole/s)	J'_q (J/s)
2	-0,597	-46,777	41,409	-8,64E+05	-0,752	-58,740	51,966	-1,10E+06
3	-1,199	-27,875	25,293	-4,96E+05	-1,517	-34,488	31,274	-6,29E+05
4	-2,345	-15,875	15,818	-2,51E+05	-3,112	-21,224	21,089	-3,46E+05
5	-4,631	-9,121	11,935	-1,11E+05	-6,216	-6,740	11,267	-6,33E+04
6	-9,099	15,661	-5,546	2,65E+05	-12,535	14,878	-1,878	2,70E+05
7	-17,845	9,490	7,302	1,68E+05	-24,743	15,240	8,245	2,41E+05
8	-32,363	24,547	6,526	2,54E+05	-44,734	45,514	-0,955	4,59E+05
9	-95,284	11,988	-3,976	3,26E+05	-71,302	60,777	7,109	3,04E+05
10	-93,174	75,647	6,968	-1,56E+05	-93,134	79,076	7,061	8,23E+04
11	-39,487	107,051	9,134	-3,32E+06	-85,687	66,622	8,808	-1,30E+05
12	-53,637	46,030	3,639	2,46E+04	-74,048	63,436	1,429	-1,00E+05
13	-35,706	29,664	0,889	-7,20E+04	-49,210	41,143	1,107	-9,47E+04
14	-18,951	16,257	0	-3,81E+04	-27,191	23,187	0,111	-5,53E+04
15	-9,828	8,403	0	-2,07E+04	-13,591	11,618	0,005	-2,85E+04
16	-4,765	4,070	0	-1,02E+04	-6,413	5,478	0	-1,37E+04
17	-2,263	1,933	0	-4,83E+03	-2,973	2,539	0	-6,35E+03
18	-1,074	0,918	0	-2,29E+03	-1,377	1,176	0	-2,94E+03
19	-0,508	0,434	0	-1,08E+03	-0,636	0,543	0	-1,36E+03

For obtaining the entropy production rate, first the forces should be calculated. For the mass forces also the liquid mole fractions are necessary. They are shown in Table 10.18.

Table 10.18: The liquid mole fractions per tray for the columns with and without heat exchangers

	without heat exchangers			with heat exchangers		
Tray	$x_{benzene}$	$x_{toluene}$	$x_{m\text{-}xylene}$	$x_{benzene}$	$x_{toluene}$	$x_{m\text{-}xylene}$
B	0,0005	0,4995	0,5			
1	0,0011868	0,6571849	0,3416283	0,0012023	0,6607318	0,3380659
2	0,0025648	0,7572157	0,2402195	0,002644	0,7651039	0,232252
3	0,0053162	0,8150852	0,1795986	0,0055374	0,8244795	0,1699832
4	0,0106823	0,8471069	0,1422108	0,011451	0,8599342	0,1286149
5	0,0212479	0,8644797	0,1142724	0,0232575	0,8700089	0,1067335
6	0,0421945	0,8305289	0,1272766	0,0471839	0,842406	0,1104101
7	0,082978	0,8067822	0,1102398	0,0941444	0,8113955	0,0944601
8	0,1566612	0,7483309	0,0950079	0,1791922	0,724563	0,0962448
9	0,310289	0,597616	0,0862846	0,3127697	0,60504	0,0821903
10	0,474831	0,4938002	0,0313676	0,4782826	0,4954453	0,0262709
11	0,6910126	0,3025955	0,0126834	0,6592202	0,3348409	0,0059377
12	0,8267587	0,1707918	0,0024481	0,8084469	0,1888696	0,0026825
13	0,9122038	0,0877962	0	0,9026602	0,0970898	0,0002489
14	0,9566953	0,0433047	0	0,9534157	0,046574	9,199E-06
15	0,9794418	0,0205582	0	0,9784213	0,0215787	0
16	0,9903966	0,0096034	0	0,9901345	0,0098655	0
17	0,9955859	0,0044141	0	0,9955478	0,0044522	0
18	0,9980459	0,0019541	0	0,9980516	0,0019484	0
19	0,9992086	0,0007914	0	0,9992066	0,0007934	0

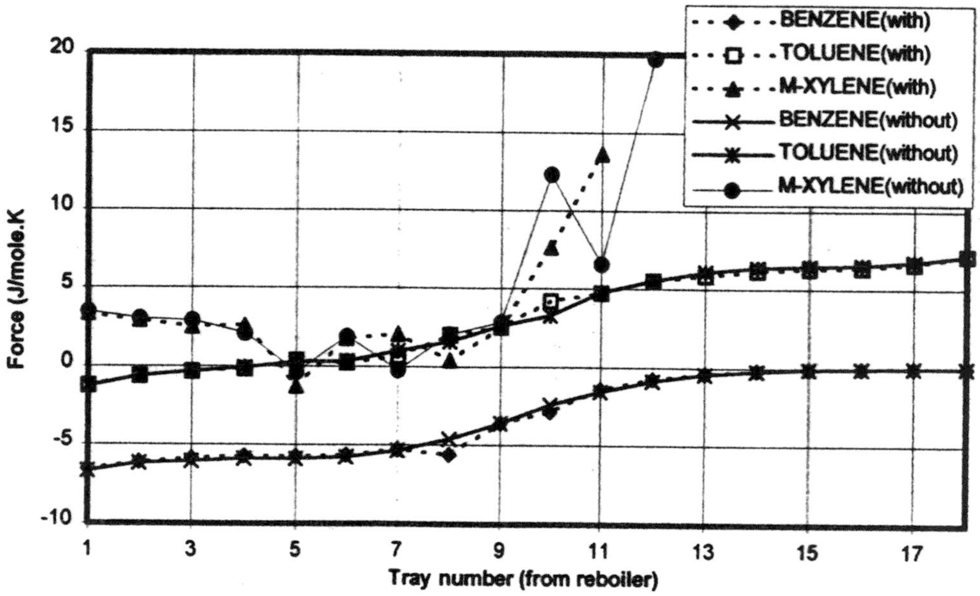

Figure 10.8 : Mass forces in the column with heat exchangers and in the column without heat exchangers

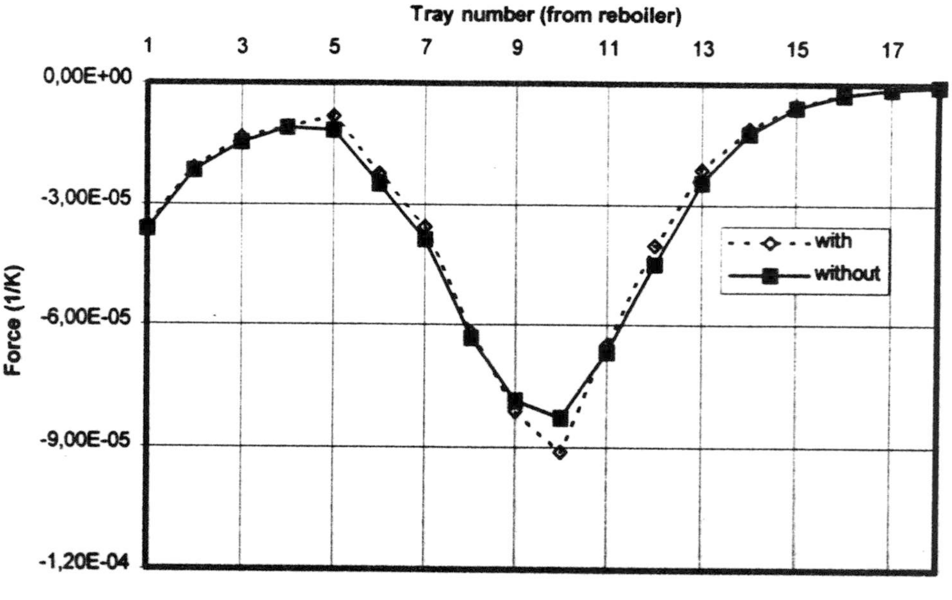

Figure 10.9 :Thermal forces in the column with heat exchangers and in the column without heat exchangers

Now it is possible to calculate the mass forces with equation (6.21), but for the thermal forces the temperature profiles of the columns are necessary. These are given in Table 10.19 and figure 10.7.

Table 10.19: The temperatures per tray for the columns with and without heat exchangers

	Temperature of the liquid (K)	
Tray	With	Without
0	392.59	392.59
1	389.23	389.15
2	387.24	387.09
3	386.03	385.85
4	385.13	384.86
5	384.17	383.95
6	383.44	382.93
7	381.34	380.60
8	377.99	377.10
9	372.09	371.86
10	365.89	365.73
11	359.71	360.50
12	356.49	356.90
13	354.63	354.83
14	353.72	353.79
15	353.27	353.29
16	353.05	353.05
17	352.95	352.95
18	352.90	352.90
19	352.87	352.87

So, now the mass and thermal forces are calculated with equation (6.21) and (6.22) and their values are given in table 10.20 and figure 10.8 and 10.9. The forces of m-xylene in the top part of the rectifying section are not given because the values of the mole fractions are below the accuracy of the simulations.

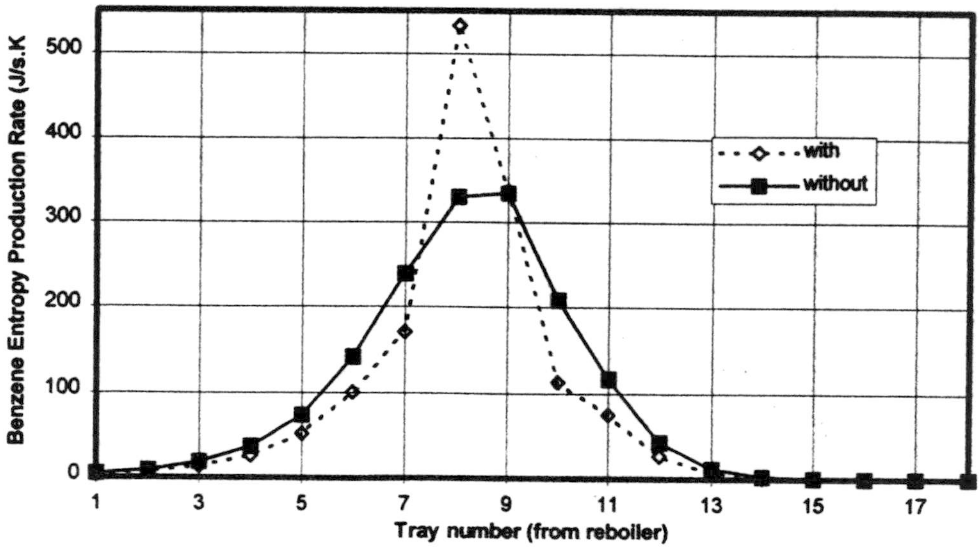

Figure 10.10 : The entropy production due to transport of benzene in the column with heat exchangers and in the column without heat exchangers

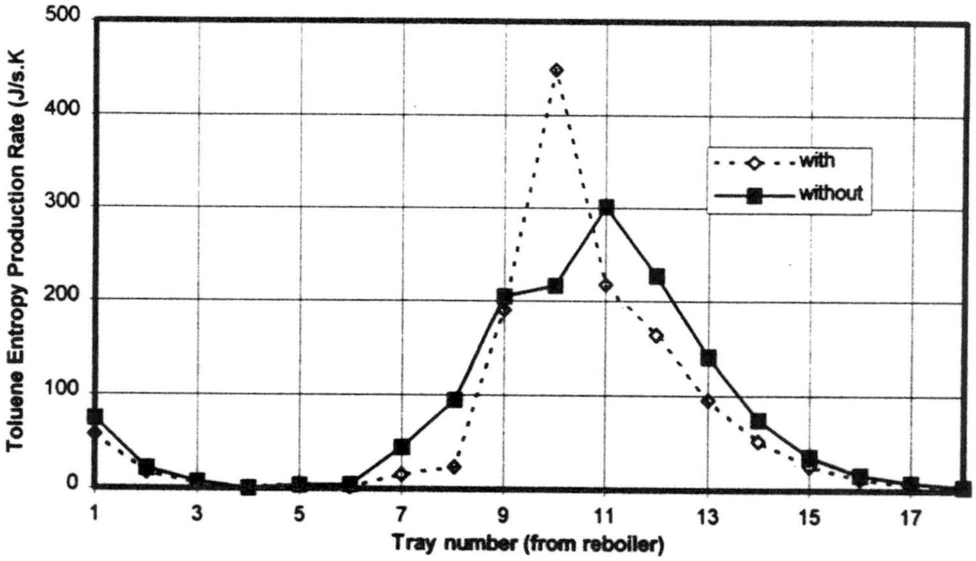

Figure 10.11 : The entropy production due to transport of toluene in the column with heat exchangers and in the column without heat exchangers

Table 10.20: The mass and thermal forces per tray for the columns with and without heat exchangers

Tray	without heat exchangers				with heat exchangers			
	$X_{benzene}$ (J/mole.K)	$X_{toluene}$ (J/mole.K)	$X_{m\text{-}xylene}$ (J/mole.K)	$X_{thermal}$ (1/K)	$X_{benzene}$ (J/mole.K)	$X_{toluene}$ (J/mole.K)	$X_{m\text{-}xylene}$ (J/mole.K)	$X_{thermal}$ (1/K)
2	-6,5163	-1,2290	3,3015	-3,52E-05	-6,6427	-1,2623	3,4475	-3,621E-05
3	-6,1055	-0,6348	2,8813	-2,1E-05	-6,1828	-0,6399	3,0066	-2,172E-05
4	-5,8221	-0,3310	2,4817	-1,344E-05	-6,0570	-0,3594	2,8693	-1,467E-05
5	-5,7265	-0,1738	2,5569	-1,099E-05	-5,8987	-0,0990	2,0774	-1,115E-05
6	-5,7108	0,3446	-1,2951	-8,237E-06	-5,8865	0,2758	-0,3891	-1,167E-05
7	-5,6244	0,2508	1,7488	-2,249E-05	-5,7445	0,3218	1,8581	-2,501E-05
8	-5,2837	0,6507	2,0092	-3,569E-05	-5,3522	0,9722	-0,2341	-3,873E-05
9	-5,5925	1,9735	0,3790	-6,196E-05	-4,6288	1,5574	2,0365	-6,325E-05
10	-3,6201	2,5156	2,5303	-8,126E-05	-3,5969	2,5900	2,8468	-7,876E-05
11	-2,8688	4,1835	7,6409	-9,124E-05	-2,4367	3,2473	12,3542	-8,274E-05
12	-1,3970	4,7256	13,6467	-6,503E-05	-1,5819	4,7513	6,5972	-6,687E-05
13	-0,7611	5,5225		-4,016E-05	-0,8637	5,5242	19,7442	-4,492E-05
14	-0,3707	5,8661		-2,135E-05	-0,4310	6,0994		-2,461E-05
15	-0,1834	6,1782		-1,107E-05	-0,2045	6,3839		-1,232E-05
16	-0,0869	6,2970		-5,361E-06	-0,0941	6,4824		-5,827E-06
17	-0,0409	6,3956		-2,556E-06	-0,0431	6,5614		-2,71E-06
18	-0,0193	6,6237		-1,224E-06	-0,0199	6,7477		-1,267E-06
19	-0,0091	7,1408		-5,92E-07	-0,0092	7,1679		-5,977E-07

The final results are the contribution of the four forces to the entropy production rate calculated by the summation of the multiplications of the force and the corresponding flux on each tray. The results are shown in Table 10.21 and figures 10.10, 10.11, 10.12 and 10.13. The statement that the assumptions for equation (6.25) are not correct, comes back in negative contributions of the thermal transport. Luckily the contribution of the thermal forces is not large. So, it has only a small effect.

Table 10.21: The mass and thermal contribution of the entropy production rate per tray for the columns with and without heat exchangers.

	without heat exchangers				with heat exchangers			
Tray	$\Delta S_{benzene}$ (J/s.K)	$\Delta S_{toluene}$ (J/s.K)	$\Delta S_{m\text{-}xylene}$ (J/s.K)	$\Delta S_{thermal}$ (J/s.K)	$\Delta S_{benzene}$ (J/s.K)	$\Delta S_{toluene}$ (J/s.K)	$\Delta S_{m\text{-}xylene}$ (J/s.K)	$\Delta S_{thermal}$ (J/s.K)
2	4,994	74,147	179,154	39,755	3,893	57,490	136,711	30,433
3	9,378	22,069	94,029	13,667	7,320	17,696	72,877	10,412
4	18,847	7,629	60,512	5,078	13,653	5,255	39,256	3,368
5	36,664	0,667	23,405	0,706	26,517	1,586	30,516	1,222
6	73,788	4,103	0,731	-3,156	51,962	5,397	7,183	-2,181
7	142,132	4,904	15,319	-6,039	100,369	2,380	12,770	-3,781
8	239,426	44,249	0,224	-17,791	170,994	15,973	13,111	-9,077
9	330,047	94,651	14,477	-19,197	532,877	23,659	-1,507	-20,194
10	334,993	204,811	20,101	-6,485	337,298	190,299	17,632	12,645
11	208,797	216,342	108,822	10,770	113,281	447,851	69,791	303,156
12	117,137	301,405	9,425	6,685	74,931	217,517	49,656	-1,601
13	42,504	227,282	21,859	4,256	27,177	163,817		2,890
14	11,718	141,429		1,361	7,024	95,366		0,813
15	2,779	74,167		0,352	1,802	51,916		0,229
16	0,604	35,511		0,080	0,414	25,629		0,055
17	0,128	16,660		0,017	0,092	12,364		0,012
18	0,027	7,935		0,004	0,021	6,078		0,003
19	0,006	3,891		0,001	0,005	3,099		0,001

The sum of all those contribution are the total entropy production rates presented in Table 10.14.

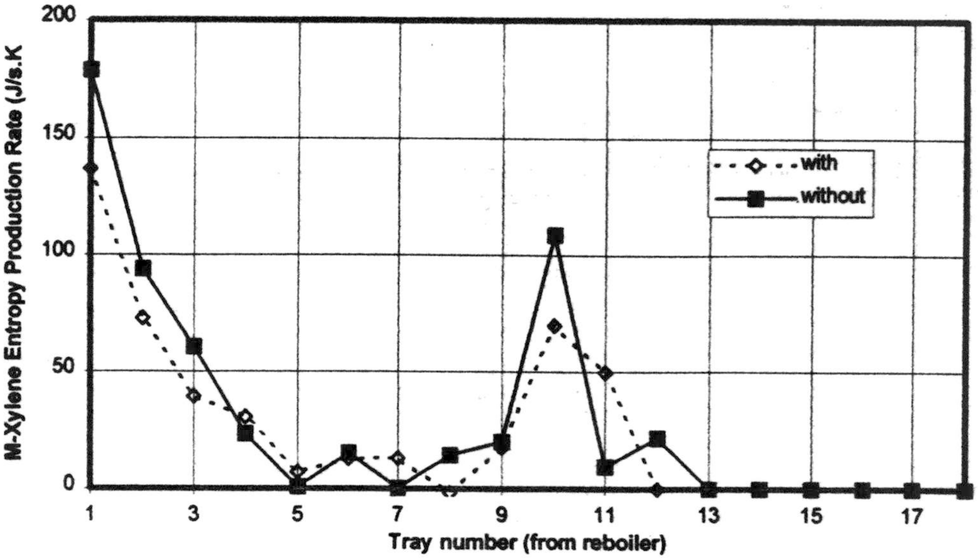

Figure 10.12 : The entropy production due to transport of m-xylene in the column with heat exchangers and in the column without heat exchangers

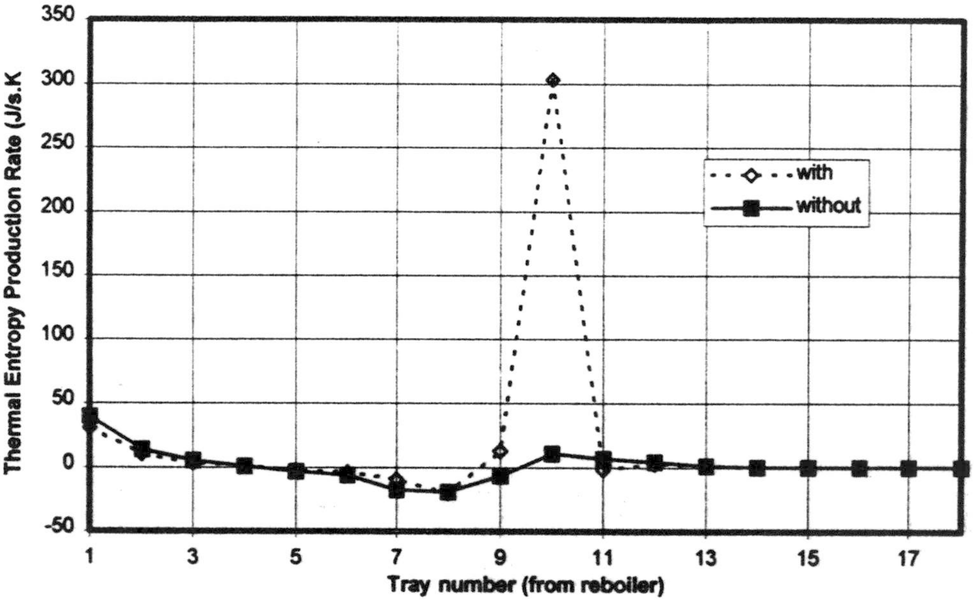

Figure 10.13 : The entropy production due to transport of heat in the column with heat exchangers and in the column without heat exchangers

The following tables (Table 10.22, Table 10.23 and Table 10.24) are the results of varying the location of the heat exchangers. The exergy loss and the deviation from the most optimal model is given for four different duties of the heat exchangers. For this optimal model the deviation of the key force form its equipartitioned force is taken, i.e. from the forces of the light key in the stripping section and in the rectifying section the deviations from the heavy key force. So, in fact the forces are splitted at the feed location. Only for the heat exchanger duty of 3.00 MW the other deviations are also given because for this duty the conclusions about the different models are made.

Table 10.22: Exergy losses and the sums of deviations at different positions of the heat exchangers with a duty of 4.0 MWatt

HXstrip	HXrect	Exloss(Watt)	Deviation (J/mole.K)
1	10	1419198	17,588
8	10	1316329	14,549
5	12	1452746	19,918
6	12	1434788	19,615
1	13	1500019	21,821
2	13	1485407	20,964
3	13	1476927	20,274
4	13	1474248	20,272
5	13	1468933	20,311
6	13	1450844	19,976
7	13	1433481	19,219
8	13	1410913	18,457
1	15	1508736	22,338
1	16	1509958	22,625
2	16	1495741	21,770
3	16	1487599	21,096
4	16	1484920	21,044
5	16	1480237	21,093
7	16	1445789	19,964
8	16	1424236	19,277
1	17	1510546	22,718
3	17	1488232	21,196
5	17	1480908	21,207
7	17	1446504	20,140

Table 10.23: Exergy losses and the sums of deviations at different positions of the heat exchangers with a duty of 3.5 MWatt

HXstrip	HXrect	Exloss(Watt)	Deviation (J/mole.K)
1	10	1431963	17,829
2	10	1412439	17,123
4	10	1400474	16,334
8	10	1336142	14,955
3	11	1445677	18,585
4	11	1438568	18,731
5	11	1433374	18,674
3	12	1471534	19,409
4	12	1464720	19,547
5	12	1460251	19,481
6	12	1447620	19,558
1	13	1504797	21,282
2	13	1492283	20,565
3	13	1484983	19,921
4	13	1478372	19,852
5	13	1475047	19,780
6	13	1460505	19,859
8	13	1422416	18,398
2	14	1497871	20,807
3	14	1490713	20,138
4	14	1484409	20,011
5	14	1481111	19,982
1	15	1513104	21,730
3	15	1493385	20,361
4	15	1487237	20,280
5	15	1483941	20,224
6	15	1469900	20,296
1	16	1514326	21,925
2	16	1501680	21,271
4	16	1488545	20,460
5	16	1485252	20,431
6	16	1471291	20,508
8	16	1434725	19,107
1	17	1514891	22,017
2	17	1502236	21,359
3	17	1495195	20,662
4	17	1489149	20,561
5	17	1485857	20,527
6	17	1471935	20,622
8	17	1435436	19,234

Table 10.24: Exergy losses and the sums of deviations for the four models of different possibilities of position of the heat exchangers with a duty of 3.0 MW.

			Deviation (J/mole.K)			
HXstrip	HXrect	Exloss(Watt)	benzene	toluene force	key force	both forces
1	10	1441677	15,404284	16,430576	17,686911	31,83486
2	10	1430068	14,709455	16,173538	16,946959	30,882993
3	10	1421594	14,187999	16,293646	16,409203	30,481644
4	10	1419662	14,115753	16,270771	16,34982	30,386524
6	10	1401154	13,977698	17,059626	16,473834	31,037324
7	10	1383772	13,23826	16,456682	15,273193	29,694941
8	10	1366974	13,306223	16,401981	15,27216	29,708205
1	11	1476777	15,472984	18,332323	19,588657	33,805306
2	11	1465373	14,776	18,114005	18,887426	32,890005
3	11	1455952	14,23411	18,195073	18,31063	32,429183
4	11	1452577	14,157523	18,445115	18,524164	32,602638
5	11	1450011	14,192112	18,227312	18,456905	32,419424
7	11	1420129	13,318709	18,034557	16,851068	31,353266
1	12	1498722	15,457925	19,132968	20,389303	34,590893
2	12	1487498	14,765568	18,886369	19,65979	33,651937
3	12	1479791	14,250601	18,985798	19,101355	33,236399
4	12	1475330	14,190886	19,122387	19,201436	33,313273
5	12	1472645	14,220967	18,944619	19,174213	33,165586
7	12	1446892	13,370721	19,180282	17,996793	32,551003
1	13	1510157	15,222692	19,470993	20,727328	34,693685
2	13	1499073	14,530294	19,240288	20,013709	33,770582
3	13	1492637	14,016123	19,39879	19,514347	33,414912
4	13	1487273	13,946177	19,290997	19,370046	33,237174
5	13	1484946	13,97395	19,12327	19,352864	33,097221
6	13	1472097	13,864468	20,058449	19,472657	33,922917
7	13	1459095	13,084573	19,434766	18,251277	32,519339
1	14	1515233	15,222458	19,654296	20,910631	34,876755
2	14	1504155	14,530046	19,434419	20,20784	33,964465
7	14	1465186	13,084299	19,608671	18,425182	32,69297
1	15	1517601	15,222197	19,863875	21,12021	35,086072
2	15	1506522	14,529795	19,636081	20,409502	34,165876
4	15	1495124	13,945652	19,683392	19,762441	33,629043
5	15	1492869	13,973422	19,513618	19,743212	33,487041
2	16	1507617	14,529588	19,805777	20,579198	34,335365
3	16	1501183	14,015489	19,908202	20,023759	33,923691
4	16	1496282	13,945467	19,825863	19,904912	33,771329
5	16	1494039	13,973239	19,653031	19,882625	33,626271
6	16	1481660	13,863749	20,566195	19,980403	34,429944
7	16	1469365	13,083729	19,98197	18,798481	33,065699
1	17	1519257	15,218279	20,103285	21,35962	35,321564
2	17	1508123	14,529506	19,873852	20,647273	34,403358
3	17	1501689	14,0154	19,982494	20,098051	33,997894
4	17	1496871	13,94152	19,908735	19,987784	33,850255
5	17	1494579	13,973129	19,738154	19,967748	33,711284
6	17	1482228	13,863611	20,667365	20,081573	34,530976
7	17	1469976	13,08358	20,082994	18,899505	33,166573
8	17	1451965	13,113482	20,096291	18,96647	33,209774

Table 10.25: Exergy losses and the sums of deviations at all positions of the heat exchangers with a duty of 2.5 MW.

HXstrip	HXrect	Exloss(Watt)	Deviation (J/mole.K)
1	10	1457376	17,573
2	10	1447726	17,045
3	10	1443554	16,492
4	10	1439322	16,659
5	10	1438431	16,592
6	10	1421290	16,348
7	10	1411841	15,475
1	11	1486031	19,369
2	11	1475502	18,679
3	11	1471222	18,509
5	11	1465490	18,259
6	11	1455430	17,389
1	12	1505105	19,992
2	12	1495424	19,356
3	12	1489904	19,100
4	12	1485382	18,747
5	12	1484049	18,823
7	12	1465087	18,082
1	13	1515472	20,302
2	13	1506227	19,681
3	13	1499993	19,200
4	13	1495994	18,921
5	13	1494139	18,960
6	13	1482650	18,879
7	13	1475076	18,203
1	14	1519949	20,390
3	14	1504576	19,326
4	14	1500623	19,015
5	14	1498779	19,125
6	14	1487550	19,018
7	14	1480058	18,349
1	15	1522030	20,535
2	15	1512652	19,956
4	15	1502791	19,184
5	15	1500959	19,279
6	15	1489843	19,206
1	16	1522994	20,671
2	16	1513597	20,069
6	16	1490904	19,322
1	17	1523440	20,736
2	17	1514033	20,128
3	17	1508186	19,700
4	17	1504258	19,383
5	17	1502424	19,477
6	17	1491395	19,387
7	17	1483997	18,728

Table 10.26: Exergy losses and the sums of deviations at all positions of the heat exchangers with a duty of 2.0 MW.

HXstrip	HXrect	Exloss(Watt)	Deviation (J/mole.K)
1	10	1474205	17,817
2	10	1466606	17,275
3	10	1461923	16,893
4	10	1458209	16,741
5	10	1456885	16,605
6	10	1446872	16,273
7	10	1437554	15,762
8	10	1420972	15,916
1	11	1497143	18,909
2	11	1489603	18,412
3	11	1485099	17,977
4	11	1480506	17,817
5	11	1479262	17,678
7	11	1464723	16,783
1	12	1512525	19,619
2	12	1504673	19,096
3	12	1500344	18,648
4	12	1495994	18,506
5	12	1494646	18,443
7	12	1479278	17,896
8	12	1464912	18,011
1	13	1520764	19,699
2	13	1513072	19,157
3	13	1508891	18,713
4	13	1504671	18,588
5	13	1502993	18,481
6	13	1494339	18,356
7	13	1487505	18,022
1	14	1524586	19,784
3	14	1512709	18,821
5	14	1506878	18,537
6	14	1498387	18,461
7	14	1491664	18,145
1	15	1526376	19,923
4	15	1510325	18,770
5	15	1508698	18,660
6	15	1500288	18,568
7	15	1493620	18,269
3	16	1515334	19,044
4	16	1511160	18,863
5	16	1509541	18,760
6	16	1501168	18,670
7	16	1494524	18,354
8	16	1480102	18,466
1	17	1527586	20,065
2	17	1519828	19,557
3	17	1515718	19,094
4	17	1511545	18,913
5	17	1509930	18,811
6	17	1501575	18,725
7	17	1494943	18,413
8	17	1480518	18,515

10.8 Manual to the C-program

In order to really do something with the program a good knowledge of the programming language C knowledge is necessary. Otherwise, only standard operations are possible and the flexibility gained with the use of such a program is lost. For a global overview of the program is referred to chapter 3.

In fact there are two versions of the program, one which performs a simulation with a feed tray based on the minimisation of the exergy loss due to mixing on the feed tray and one where the feed tray is given in the datafile with the initialisation parameters. This file is called for the version with the variable feed tray location called feedinit.dat and for the version with an automatic feed tray analysis called init.dat.

Besides a variable feed tray or not the initialisation parameter file contains:

1. The number of points in the grid for one component. The reciprocal of this value is the gridwidth.
2. The number of components with increasing volatility.
3. The names of the components in the notation as used in Aspen Plus.
4. The pressure in bars.
5. The feed flow in mole/s.
6. The liquid mole fraction of the components except for the heaviest component. This one is calculated in the program.
7. The number of the light key component in the row of increasing volatility.
8. The factor with which the minimum reflux ratio is multiplied.
9. The feed tray (if this is the version which needs it)
10. The location of the heat exchanger in the stripping section. If no heat exchanger is used a negative value should be given.
11. The duty of the heat exchanger in the stripping section in megawatts. If no heat exchanger is used zero should be given.
12. The location of the heat exchanger in the rectifying section. If no heat exchanger is used a negative value should be given.
13. The duty of the heat exchanger in the rectifying section in megawatts. If no heat exchanger zero is used should be given.

The last four parameters are not available for the version with a variable feed tray. All these parameters can be changed without compiling the program again. But if something is changed in the program, it should be compiled with the following command:

```
gcc -o <name>.out <name>.c -Wall -lm
```

The command gcc is the universal command for compiling a C program. The extension -o gives the opportunity to give the executable another name than a.out. Remind that an executable always has the extension '.out' and the source '.c'. The extension -Wall gives besides all the possible errors also all the warnings. The extension -lm enables the use of various mathematical functions. A few of them are used in the program.

10.9 Alternative calculation method with Aspen Plus

These simulation can also be done with Aspen Plus, but it is more time consuming. This appendix will suggest a calculation method with Aspen Plus.

The first step is the creation of an input file of a distillation column with the model manager of Aspen Plus. This is done by defining one column with all the specifications necessary in a flowsheet. When this flowsheet is saved, one of the files is called the input file and is described by '<runID>.inp'. It contains all the instructions for Aspen Plus. The runID is the name of the saved simulation. The same calculation done with the model manager can be done with the following command:
aspen <runID>

The second step is to make Aspen Plus flexible by writing a program in a programming language like C or FORTRAN, which is able to create and run this input file. The big advantage now is that an unlimited amount of calculations can be done without changing the settings manually. After each calculation the results should be read and saved into data files. The summary file toolkit is able to do this. This toolkit is a set of FORTRAN routines which are able to read the summary file. This summary file is also a result of the simulation and is described by '<runID>.sum'. As already mentioned in chapter 3.1, the summary file toolkit is also used in this project. The source code in FORTRAN is given here as an example:

```
c    variable declarations

     IMPLICIT REAL*8 (A-H, O-Z)
     CHARACTER*80 RCPROP, RCUNIT, ASPSUP
     CHARACTER UNISET*4, VERSN*20, RUNID*8, DATE*80, INFILE*80, TYPE*12
     CHARACTER TABID*8, PNAME*12, SUBSID*8, PHASE*8, COMPID*8, WETDRY*4
     CHARACTER BASIS*4, LABEL*16
     REAL MATRIX

     DIMENSION MATRIX(15,11000)
     DIMENSION RVALS(11000),PNAME(15), PHASE(15), COMPID(15),SUBSID(15), WETDRY(15)

c    Expanding environment  variables

     CALL GETENV('ASPDIR',ASPSUP)
     DO 10 I = 80, 1, -1
       IF(ASPSUP(I:I) .NE. ' ') GO TO 15
 10  CONTINUE
 15  CONTINUE
     RCPROP = ASPSUP(1:I) // '/asptool/rcpropnu.dat'
     RCUNIT = ASPSUP(1:I) // '/asptool/rcunits.dat'

c    open <runid>.sum file

     OPEN(2,FILE='table.sum',STATUS='UNKNOWN')
     OPEN(10,FILE='OUT0.DAT',STATUS='UNKNOWN')
     OPEN(20,FILE='OUT1.DAT',STATUS='UNKNOWN')
     OPEN(30,FILE='REF.DAT',STATUS='UNKNOWN')

c    call TKINIT AN TKINIFO  and check for errors21

     RMISS = 1E21
     UNISET = 'SI'
     CALL TKINIT(UNISET, 1, 2, 3, RCPROP, 4, RCUNIT, RMISS, IERR)
     IF (IERR .NE. 0) WRITE(*,*) 'ERROR IN TKINIT'
     CALL TKINFO( VERSN, RUNID, DATE, INFILE, ISSTAT, ISTAT, NBLOCK, NSTRM, NTABLE, NSENS)
```

```
      WRITE(*,*) VERSN, RUNID, DATE, INFILE, ISSTAT, ISTAT, NBLOCK, NSTRM, NTABLE, NSENS

C     call the table 1 AND 2 with the VLE data


      ITABLE=1
      CALL TKNPPT(ITABLE, TABID, TYPE, IERR)
      WRITE(*,*) TABID, TYPE
      IF (IERR .NE. 0) WRITE(*,*) 'ERROR IN TKNPPT'
      CALL TKSPPT(TABID, NPOINT, NPROP, IERR)
      WRITE(*,*) NPOINT, NPROP
      IF (IERR .NE. 0) WRITE(*,*) 'ERROR IN TKSPPT'


      DO 400, J=2, NPROP
        DO 300,K=1,NPOINT
          CALL TKNPPR(TABID, NPOINT, J, PNAME, SUBSID, PHASE, COMPID, WETDRY, BASIS, RVALS, TYPE,
LABEL, IERR)
          MATRIX(J,K)=RVALS(K)

 300    CONTINUE
 400  CONTINUE


      DO 800, K=1, NPOINT
        DO 700,J=2,NPROP
          WRITE(10,500) MATRIX(J,K)
 500        FORMAT(F20.5)

 700    CONTINUE
 800  CONTINUE


      ITABLE=2
      CALL TKNPPT(ITABLE, TABID, TYPE, IERR)
      WRITE(*,*) TABID, TYPE
      IF (IERR .NE. 0) WRITE(*,*) 'ERROR IN TKNPPT'
      CALL TKSPPT(TABID, NPOINT, NPROP, IERR)
      WRITE(*,*) NPOINT, NPROP
      IF (IERR .NE. 0) WRITE(*,*) 'ERROR IN TKSPPT'


      DO 1000, J=2, NPROP
        DO 900,K=1,NPOINT
          CALL TKNPPR(TABID, NPOINT, J, PNAME, SUBSID, PHASE, COMPID, WETDRY, BASIS, RVALS, TYPE,
LABEL, IERR)
          MATRIX(J,K)=RVALS(K)

 900    CONTINUE
 1000 CONTINUE


      DO 1200, K=1, NPOINT
        DO 1100,J=2,NPROP
          WRITE(20,500) MATRIX(J,K)

 1100   CONTINUE
 1200 CONTINUE


C     call table 3 with the REFERENCE  data

      ITABLE = 3
      CALL TKNPPT(ITABLE, TABID, TYPE, IERR)
      WRITE(*,*) TABID, TYPE
      IF (IERR .NE. 0) WRITE(*,*) 'ERROR IN TKNPPT'
      CALL TKSPPT(TABID, NPOINT, NPROP, IERR)
      WRITE(*,*) NPOINT, NPROP
      IF (IERR .NE. 0) WRITE(*,*) 'ERROR IN TKSPPT'


      DO 1400, J=2, NPROP
```

```
      DO 1300,K=1,NPOINT
        CALL TKNPPR(TABID, NPOINT, J, PNAME, SUBSID, PHASE, COMPID, WETDRY, BASIS, RVALS, TYPE,
LABEL, IERR)
        MATRIX(J,K)=RVALS(K)

1300   CONTINUE
1400 CONTINUE


    DO 1800, K=1, NPOINT
      DO 1700,J=2,NPROP
        WRITE(30,500) MATRIX(J,K)

1700   CONTINUE
1800 CONTINUE

    CLOSE(10)
    CLOSE(20)
    CLOSE(30)

    END
```

□

The compiling of this program was done by the following set of instructions, in which the name of the executable and source file should be filled in:

```
EXENAME = <name of the executable>
FFLAGS = -c -e
LIBS=-lm
TOOLLIB=/opt2/aspen/ap921/asptool/toolkit.a
<name of the source>   : <name of the source>.o
        f77 <name of the source>.o $(TOOLLIB) -o $(EXENAME) $(LIBS)
<name of the source>.o   : <name of the source>.f
        f77 $(FFLAGS) <name of the source>.f
```

Note that the location of the libraries of the summary file toolkit(called TOOLLIB) depends on the computer/network used.

As this summary file toolkit is written in FORTRAN it is perhaps more convenient to write the total program also in FORTRAN. But the knowledge of this language should be available of course.

10.10 Aspen Plus input files

This appendix contains the two input files of the Aspen Simulations used for this project. The first is an example of the input file fro creating the grids and the second is the input file used for as a benchmark for the simulations of the program.

10.10.1 Input file for the creation of the grids

```
TGS


TITLE 'table'

IN-UNITS SI

DIAGNOSTICS
   TERMINAL SIM-LEVEL=0 CONV-LEVEL=0 COST-LEVEL=0 PROP-LEVEL=0  &
      ECON-LEVEL=0 STREAM-LEVEL=0 SYS-LEVEL=0
   MAX-PRINT SIM-LIMIT=15000

RUN-CONTROL MAX-ERRORS=15000

DATABANKS PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
      NOASPENPCD

PROP-SOURCES PURECOMP  / AQUEOUS  / SOLIDS  /INORGANIC

COMPONENTS
   1 BENZENE 1 /
   2 TOLUENE 2 /
   3 M-XYLENE 3

PROPERTIES UNIQ-RK
   PROPERTIES IDEAL

PROP-REPLACE IDEAL UNIQ-RK

PROP-SET TEST1 MOLEFRAC HMX SMX TEMP SUBSTREAM=MIXED PHASE=L V

PROP-SET TEST2 MOLEFRAC HMX SMX SUBSTREAM=MIXED

PROP-TABLE PT-1 FLASHCURVE
   MOLE-FLOW 1 1 / 2 1 / 3 1
   STATE PRES=1.0000 <BAR> VFRAC=0
   VARY MOLE-FRAC COMP=1
   RANGE LOWER=0 UPPER=1 NPOINT=10
   VARY MOLE-FRAC COMP=2
   RANGE LOWER=0 UPPER=1 NPOINT=10
   TABULATE PROPERTIES=TEST1

PROP-TABLE PT-2 FLASHCURVE
   MOLE-FLOW 1 1 / 2 1 / 3 1
   STATE PRES=1.0000 <BAR> VFRAC=1
   VARY MOLE-FRAC COMP=1
   RANGE LOWER=0 UPPER=1 NPOINT=10
   VARY MOLE-FRAC COMP=2
   RANGE LOWER=0 UPPER=1 NPOINT=10
   TABULATE PROPERTIES=TEST1

PROP-TABLE PT-3 FLASHCURVE
   MOLE-FLOW 1 1 / 2 1 / 3 1
   STATE TEMP=298.15 PRES=1 <BAR>
   VARY MOLE-FRAC COMP=1
   RANGE LOWER=0 UPPER=1 NPOINT=10
   VARY MOLE-FRAC COMP=2
   RANGE LOWER=0 UPPER=1 NPOINT=10
   TABULATE PROPERTIES=TEST2
```

10.10.2 Input file for the benchmark column

```
IN-UNITS MET VOLUME-FLOW='CUM/HR' ENTHALPY-FLO='MMKCAL/HR' &
HEAT-TRANS-C='KCAL/HR-SQM-K' PRESSURE=BAR TEMPERATURE=C &
VOLUME=CUM DELTA-T=C HEAD=METER MOLE-DENSITY='KMOL/CUM' &
MASS-DENSITY='KG/CUM' MOLE-ENTHALP='KCAL/MOL' &
MASS-ENTHALP='KCAL/KG' HEAT=MMKCAL MOLE-CONC='MOL/L' &
PDROP=BAR

DEF-STREAMS CONVEN ALL

DATABANKS PURECOMP / AQUEOUS / SOLIDS / INORGANIC / &
        NOASPENPCD

PROP-SOURCES PURECOMP / AQUEOUS / SOLIDS / INORGANIC

COMPONENTS
  A C6H6 A /
  B C7H8 B /
  C C8H10-2 C

FLOWSHEET
  BLOCK B2 IN=1 OUT=2 3

PROPERTIES UNIQ-RK

STREAM 1
  SUBSTREAM MIXED PRES=1 VFRAC=0 MOLE-FLOW=100 <MOL/SEC>
  MOLE-FRAC A 0.5 / B 0.25 / C 0.25

BLOCK B2 RADFRAC
   IN-UNITS SI
   DESCRIPTION "test"
    PARAM NSTAGE=18
    FEEDS 1 9
    PRODUCTS 2 1 L / 3 18 L
    P-SPEC 1 1 <BAR>
    COL-SPECS MOLE-RDV=0 MOLE-D=.0505000 MOLE-BR=9.163
```