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**Complex evaluation methodology for energy-integrated
distillation columns**

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Abstract

Distillation is the primary separation process used in the chemical process industry for liquid mixtures separation. Apart from the numerous advantages of the distillation, it has a drawback, namely its significant energy requirement. In order to reduce the energy consumption of these systems energy integration is applied within the distillation columns or with other units of the global process. The specific literature offers a large number of solutions for energy integration.

During the process design it is important to select the best applicable energy integration for the distillation system in the case of the given separation task. In the last decades the set of the selection criteria was completed with new elements. Apart from the economic criterion, nowadays the environmental consciousness and controllability are also important parameters of the process design.

The primary motivation of this thesis is to elaborate a complex process design methodology that evaluates the distillation systems based on exergetic, economic and greenhouse gas (GHG) emission aspects. The aim of the methodology is to determine how these three features should be applied in process design to obtain information about the accuracy of the design alternatives. The methodology is tested and demonstrated on three different energy-integrated distillation systems: the direct sequence with backward heat-integration (DQB), fully thermally coupled distillation column (FTCDC), and sloppy distillation system with forward heat-integration (SQF). The studied distillation systems are compared to each other and to the non-integrated conventional arrangement in the case of the separation of ternary mixtures. Applying the proposed methodology reveals that among the investigated distillation schemes the heat-integrated DQB alternative proves to be the best applicable since it shows the most favoured features in a wide and flexible range. The application of the methodology on the energy-integrated distillation proofs the accuracy of the complex evaluation methodology. On the other hand, it highlights and demonstrates that the exergy analysis can predict the results of the economic study and the environmental evaluation to make the decisions, associated with process design, much simpler.

Based on the results of the energy-integrated distillation system investigation the backward heat-integrated distillation system is proposed during the retrofit design of an industrial N, N-dimethylformamid (DMF)-water separation system. The task was to examine how the capacity of the distillation based separation system could be increased by 42.8% of a distillation system consisting three columns. The performance of the existing distillation system and various increased-capacity structures have been studied using rigorous process simulation. As the results of the study shows, the proposed energy integration results in significant energy savings. The energy-integrated separation system of increased-capacity consumes about half of the energy that would be required for the operation of the non energy-integrated system.

The secondary motivation of my work is to investigate the controllability features of the energy-integrated distillation systems and to elaborate an easy applicable controllability analysis method in order to compare energy-integrated distillation systems based on their control properties and to select the easiest controllable one.

The proposed controllability analysis is applied on the investigated energy-integrated distillation systems and the results of this comparative study show that DQB has the best control features among the studied ones. The second best is the FTCDC and it is followed by the SQF. However, the conventional direct distillation sequence without energy integration is considered a simple configuration, its controllability features prove to be worse than the studied energy-integrated distillation systems. The results of the controllability analysis are verified with closed-loop simulations by carrying out load rejection analysis. It can be concluded that the results of the two different analysis methods are in good agreement.

The application of the proposed controllability analysis sustains that the method is simple and fast, thus it can be used in the early stage of process design.

Table of Contents

Chapter 1	Introduction.....	7
1.1	Motivation and focus	7
1.2	Approach.....	8
1.3	Overview of the dissertation	9
Chapter 2	Literature review	10
2.1	Distillation.....	10
2.2	Energy-integrated distillation systems	12
2.3	Thermodynamic efficiency of the distillation systems	14
2.4	Environmental emission estimation	15
2.5	Controllability issues and dynamic behaviour	17
2.5.1	Condition number (CN)	20
2.5.2	Morari resiliency index (MRI).....	20
2.5.3	Relative Gain Array Number (RGAno).....	20
Chapter 3	The investigated case studies.....	24
3.1	The studied energy-integrated distillation systems.....	24
3.1.1	Direct sequence with backward heat integration (DQB)	24
3.1.2	Fully thermally coupled distillation column (FTCDC).	25
3.1.3	Sloppy distillation system with forward heat integration (SQF)	26
3.1.4	Conventional direct distillation scheme (Conv. Dir.)	27
3.2	Separation tasks	28
Chapter 4	The proposed complex evaluation methodology	29
4.1	Introduction.....	29
4.2	Definition of the evaluation methodology	29
4.3.	The first level of the methodology.....	30
4.3.1	The elaboration of the process alternatives.....	31
4.3.2	Definition of system boundaries	31
4.3.3	Selection of input / output parameters	31
4.4	The second level of the methodology	31
4.4.1	Collection of the necessary data	31
4.4.2	Exergy analysis	32
4.4.3	Economic Study	34
4.4.4	Greenhouse gas emission estimation	34
4.5	The third level of the methodology.....	35
4.5.1	Ranking process alternatives based on desirability function	36
4.5.2	Decision	37
4.6	Application of the proposed evaluation methodology on the studied distillation systems.....	37
4.7	Conclusions of the complex evaluation methodology application	49

Chapter 5	Retrofit design of an industrial heat-integrated distillation system...	51
5.1	Introduction.....	51
5.2	The aim of the retrofit design work	52
5.3	Description of the existing separation process.....	52
5.4	Simulation of the existing separation process.....	54
5.5	Retrofit scenarios and calculations	57
5.5.1	Existing vacuum columns	59
5.5.2	Extra column connected parallel to the vacuum columns	60
5.5.3	Atmospheric column.....	60
5.6	Suggested retrofit design.....	61
5.7	Conclusions.....	64
Chapter 6	Operability evaluation of the energy-integrated distillation systems.	65
6.1	Controllability analysis of the distillation systems	66
6.1.1	The selection of the controlled and manipulated variables.....	66
6.1.2	Calculation of the controllability indices in frequency domain.....	66
6.1.3	Aggregation of the controllability indices	67
6.1.4	Ranking of the studied distillation systems	68
6.2	Application of the controllability analysis on the investigated distillation systems.....	68
6.3	Conclusion	78
Chapter 7	Major new results	79
Thesis 1	79
Thesis 2	79
Thesis 3	80
Thesis 4	80
List of Publications	81
References	85
Nomenclature	88
List of figures	91
List of tables	92
Appendix A	93
Appendix B	95

Chapter 1

Introduction

“Distillation, King in separation, will remain as the workhorse separation device of the process industries. Even though it is old in the art, with a relatively mature technology support base, it attracts research and professional interest. Without question, distillation will sail into future with clear skies and a strong wind. It will remain the key separation method against which alternate methods must be judged.” Dr. James R. Fair, 1990

In this chapter the thesis is presented concisely and placed in a wider perspective. The motivations of my work are summarized and the approach is described. At the end of this chapter an overview of the thesis is given. The literature background and the related works are discussed in Chapter 2.

1.1 Motivation and focus

The chemical process design practice has developed over the years according to the requirements of the time. The aim of the process design is to find the feasible process alternatives and to choose the most suitable one for the specific production task. This process design became computer aided in the last decades which makes possible to apply more complex analysis in the early stage of design. Within the computer aided conceptual design two major approaches are elaborated: the hierarchical approach, and the algorithmic design approach. These approaches help to find the optimal process alternative by working out the heat and material balances, operating conditions, and process equipment performances. Parallel to the design of the process further studies are needed in order to eliminate process alternatives outside the limits of the operating conditions, profitability or safety conditions. Further benefit of comprehensive process evaluation in early stage is that the late modifications with high cost can be avoided.

Thus, the methodology of process design used in the past decades should be reconsidered and developed according to the criteria claimed by recent requirements.

The early stage of process design was practically based on engineering design and the alternatives were evaluated merely according to their economic features. The methodology of process design should be completed with new steps. Nowadays, due to increasing energy prices and strict environmental regulations the investigation of the energy efficiency and the emissions of the process must take place simultaneously at the early stage of process design.

The demand for energy has been continuously increasing for years and operation units with large energy demand have become more difficult to be supplied. The energy efficiency of a system becomes an important criterion during retrofitting and design of industrial processes. On the other hand, the emission regulations constrain engineers to consider the concept of environmentally-consciousness in their work. This environmentally-consciousness is even more important in the European Union since the Union ratified the Kyoto Protocol and established a scheme for greenhouse gas emission trading in 2005. Due to the large energy demand of distillation systems these regulations have special importance which can be reduced e.g. by using energy integration.

The thesis presents an evaluation methodology for energy-integrated distillation columns which investigates the distillation system based on exergy analysis, economic study, and greenhouse gas emission estimation. As a next step of the process design the controllability and dynamic behaviour of the distillation systems are investigated. These investigation steps assure the designer that the distillation system will meet the claimed requirements.

The proposed methodology should be included in the global process synthesis beside of the preliminary evaluation of the market, development of data necessary for the design, and detailed engineering design.

1.2 Approach

The simulation models of the studied distillation systems are implemented in the ASPEN Plus process simulator. Moreover, the applied studies in this work e.g. exergy analysis,

economic study require the use of MS-Excel connected to the process simulator where the different exergy calculating equations or the cost functions are introduced.

The environmental impact assessment in the dissertation is done with the use of SimaPro software. The model developed by Gadalla et al verifies the results calculated by this software. The controllability study is carried out with the Control Design Interface of Aspen Dynamics and the results are further analysed in Matlab.

In order to model the distillation systems the following simulation methodology is developed: first, the number of the theoretical trays, location of the feed trays and the reflux ratio are estimated with shortcut design procedure. The results of the shortcut design are implemented in rigorous column model.

The model of the distillation system composed by two columns is simulated first without energy integration and based on the energy-demand the energy integration between the two columns is applied. Furthermore, the energy consumption of the distillation system is optimized. The applied process simulator is used also for equipment sizing such as distillation column diameter, tray geometry, and heat exchanger dimensions.

1.3 Overview of the dissertation

The remainder of this thesis is as follows:

In chapter 2 the literature review is presented in connection with my work in topic.

The chapter 3 presents the investigated distillation systems as case studies and the separation tasks.

The chapter 4 elaborates a complex evaluation methodology for energy-integrated distillation systems. The proposed methodology is applied on the distillation systems presented in the previous chapter

An industrial retrofit design is presented in the chapter 5. The task of the retrofit design is to increase capacity by 42.8% and energy saving.

Chapter 6 presents operability evaluation of the energy-integrated distillation system regarding controllability and dynamic behaviour.

Chapter 2 Literature review

Distillation is a widely used separation process, which separates liquid mixtures formed by components with different volatilities. The group of separation processes can be classified according to the type of feed stream (heterogeneous or homogeneous).

Homogeneous feed can be classified based on the type of controlling process either equilibrium process or rate governed process, the equilibrium process can be classified depending on the type of separating agent (energy or mass). The energy is used as separating agent in distillation, evaporation and crystallization processes. Mass separating agent is used in the case of absorption, stripping, and extraction. The previously mentioned rate governed process class contains unit operations such as reverse osmosis, gaseous diffusion, electro dialysis, and gas permeation.

Heterogeneous feed is generally separated by mechanical separation processes as filtration, flotation, and centrifuge.

In this thesis the distillation is selected as separation process in case of zeotropic ternary mixtures. In the case of regular distillation the separation is occurring by adding a separating agent, which takes the form of matter or energy.

The disadvantage of the distillation is its high energy consumption which involves high operating cost for these separation units. Significant energy savings can be made with use of distillation structures with energy integration such as heat integration, heat pumping, and thermocoupling.

2.1 Distillation

Distillation is a key separation technology in the chemical industries for the separation of liquid mixtures. It is a process of separating the liquid mixture into two or more products that have different boiling points by boiling out the more volatile components out of the mixture. In spite of its low thermodynamic efficiency the popularity of the distillation has not decreased in the last decades. The advantage of the distillation has both kinetic and thermodynamic reasons: it takes place without added inert material and the mass transfer

per unit volume in distillation is limited only by the diffusional resistances, thus the distillation has the potential for high mass transfer rates and proportionally it involves low capital costs. The distillation can not be used or not economic in the cases when:

- The difference of the volatility between the components is small.
- A small quantity of high boiling point component is to be recovered from feed and the whole feed has to be vaporized because of this small quantity.
- A compound is not stable thermally even under vacuum conditions.
- The mixture is extremely corrosive or highly fouling.

The distillation design can not be discussed without mentioning the vapour-liquid equilibrium (VLE). However VLE is a large topic and the detailed discussion is not the aim of the thesis so a brief and practical state-of-the-art review is presented of the VLE topic.

The K-value is a measure of the tendency of component i to vaporize:

$$K_i = \frac{\text{Mole of fraction of component } i \text{ in vapor phase}}{\text{Mole of fraction of component } i \text{ in liquid phase}} \quad (1)$$

The high K-value shows that the component tends to concentrate in the vapour phase and the low K-value indicates that the component tends to concentrate in the liquid phase. If the K-value is unity, the component will split equally between the vapour and liquid phase. The K-value is a function of temperature, pressure, and composition.

Apart from the K-value, the relative volatility can be use to characterize the liquid mixture:

$$\alpha_{ij} = \frac{K - \text{value of component } i}{K - \text{value of component } j} \quad (2)$$

Distillation is a technique of separating components according to their relative volatility which is a measure of the ease of separation. If relative volatility is high, one component has a much greater tendency to vaporize than the other and the mixture can be easily separated e. g. by distillation. In the case of relative volatility close to unity the mixture can not be separated by distillation.

The ease of separation of ternary mixtures (ABC) can be characterized by the separation index (SI):

$$SI = \frac{\alpha_{AB}}{\alpha_{BC}} \quad (3)$$

where α_{ij} is the relative volatility.

If $SI < 1$ A/B separation is more difficult than B/C separation. If $SI \sim 1$ A/B separation is as difficult as B/C separation, the ease of separation is balanced. If $SI > 1$ the B/C separation is more difficult than A/B separation.

The present thesis contains case studies separating ideal mixtures. In these ideal mixtures the components have similar physicochemical properties with equal intermolecular forces between the molecules. The VLE for an ideal mixture can be defined as:

$$y_i P = x_i \gamma_i(T, x) P_i^0(T) \quad (4)$$

where

x_i, y_i – the vapour and liquid mole fractions of component i

P - pressure

T – temperature

P_i^0 – saturated vapour pressure of component i

γ_i – activity coefficient of component i in liquid phase

The activity coefficient is a measure of non-ideality of a mixture and changes both with temperature and composition. In the case of ideal mixtures the value of activity coefficient is unity.

2.2 Energy-integrated distillation systems

The demand for energy has been continuously increasing for years and operation units with large energy demand have become more difficult to be supplied. Reconsideration and rationalization of industrial plants is recommended. On the other hand reducing energy requirements of distillation systems leads to lower CO₂ emission; this is why the plant designer must take the different energy saving solutions in account and choose the adequate distillation system for the specific separation task.

The large energy requirement of distillation can be reduced by using different types of energy integration between the distillation columns. Among the energy-integrated solutions several alternatives can be mentioned:

- i. Heat integrated columns
 - Conventional heat integration
 - Forward heat integration
 - Backward heat integration
 - Sloppy sequence with heat integration
 - Forward heat integration
 - Backward heat integration
 - Partial heat-integrated alternatives
- ii. Thermo coupling
 - Fully thermally coupled distillation column or Petlyuk column
 - Divided wall column or Kaibel column
 - Side stream rectifier
 - Side stream stripper
- iii. Heat pumping
 - Vapour recompression
 - Bottom flash
 - Closed cycle or working fluid
- iv. Energy integration of the distillation columns with the overall process

Even today, the most frequently studied energy consuming process in the chemical industry is the separation systems based on distillation. The large energy requirement of these processes can be reduced by using energy integration.

This thesis studies representative distillation systems of the heat-integrated and the thermocoupling group. These energy-integrated distillation systems are frequently studied in the literature¹⁻⁷, investigating their energy saving properties through comparative studies, elaborating design methods for one specific type of energy-integrated distillation sequence. Sobocan et al⁸ developed a systematic synthesis of thermally integrated distillation systems. This method helps in reducing external energy input of the distillation systems by minimizing the utility consumption and maximizing the heat exchange between the integrated columns. The elaborated algorithmic procedure uses the extended grand composite curve in order to select the most adequate heat-integrated

distillation system. The proposed design method takes in account only energetic criteria. A completely different approach is developed by Wang et al⁹ for distillation system synthesis. The authors propose an improved genetic algorithm, on which a rigorous model for synthesis and optimization of a distillation system is set up. The proposed approach does not rely on a sequential decomposition of the problem since it accounts simultaneously for the trade-off between energy cost and separation sequence.

Mascia et al¹⁰ examines different heat-integrated and thermally coupled distillation systems. The authors carry out a comparative study of the investigated distillation systems and rate these systems based on their total annual cost. Apart from the economic evaluation, this rating does not contain any other criterion.

Annakou et al¹¹ have studied heat-integrated schemes and fully thermally coupled distillation columns (FTCDC) by rigorous modelling and compared them to conventional schemes. They have found that FTCDC can be competitive with the heat-integrated schemes only in those cases when the concentration of the middle component is high and the A/B split is harder than B/C split otherwise FTCDC is less economic than the heat-integrated scheme.

Regarding the energy demand of the thermally coupled distillation columns Hernandez et al.¹² have studied the Petlyuk column and six alternative arrangements for ternary hydrocarbon mixture separation. They have found that the alternative distillation systems have very similar values of energy demands and thermodynamic efficiencies.

2.3 Thermodynamic efficiency of the distillation systems

The large energy demand of the distillation urges to study the process and to identify the energy losses. Certainly, the low thermodynamic efficiency of distillation is caused not by the separation process but mainly by the work necessary to introduce and remove the heat from the column¹³. Thermodynamically, the distillation process consists of the removal of entropy of mixing. The process requires exergy or work of separation. In a distillation process, exergy is provided by the input and the removal of heat at different temperature levels. Heat at high temperature is fed into the reboiler and heat at low temperature is removed in the condenser. Efficiency of distillation columns is very low

because the actual exergy needed for a separation is much larger than the exergy for reversible separation.

In order to investigate the energy wastes, a useful tool is the exergy analysis, which gives an overall view about the location and scale of energy losses in the process. Some published works in literature focus on development of exergy analysis methods and expressive parameters in order to quantify and represent the lost energy and the thermodynamic efficiency of the distillation columns¹⁴⁻¹⁸. Other research works similar to this one, apply the basic equations of the second law of thermodynamics and calculate the thermodynamic efficiency for different distillation systems^{19,20}.

Suphanit et al. use successfully the exergy loss profile combined with the real column T-H profile in order to locate the heat transfer across the wall of the dividing-wall distillation column. The exergy analysis can be applied also for the study of complex distillation plants to identify the process sections with the highest exergy losses and to locate process sections with exergy improvement potential^{20,21}.

2.4 Environmental emission estimation

The emission inventory of distillation systems may contain air pollutants and residual wastes. The former is produced through the heat generation and because of the large energy demands of the distillation systems the quantity of air pollutants is significant. The quantity of the emission related to the residual wastes depends on the separated mixture. The air pollutants released by the heating system of the distillation may contain carbon-, nitrogen-, sulphur-, and halogen-containing compounds. The quality and quantity of these pollutants depend on the type of the fuel used for heating. In the case of the fossil fuels the major part of the emission is formed by the carbon dioxide (CO₂). Thus, the air pollutant emission related to distillation systems contribute to the global warming. Present-day measurements demonstrate the global increases in the concentration of gases such as carbon dioxide, methane, and nitrous oxide in the atmosphere. These greenhouse gases (GHG) act as atmospheric thermal isolators. They absorb infrared radiation from the surface of the Earth and reradiate a portion of this radiation back to the surface.²² These pollutants have a residence time that means how long a representative molecule of the substance will stay in the atmosphere before it is

removed. In order to express the contribution of different gases in global warming the global warming potential (GWP) was defined. The GWP is a quantified measure of the globally averaged relative radiative forcing impacts of a particular greenhouse gas. It is defined as the ratio of the time-integrated radiative forcing from the instantaneous release of 1 kilogram (kg) of a trace substance relative to that of 1 kg of a reference gas (CO₂). Thus, the GWP depends on the absorption of infrared radiation by a given substance, the spectral location of its absorbing wavelengths, and the atmospheric lifetime of the substance.

The use of energy efficient distillation is beneficial also from the point of view of greenhouse gas emission since this emission is limited in most of the countries. The CO₂ emission of distillation systems is investigated by Gadalla et al^{23, 24}. The authors quantify the CO₂ emission for a propylene-propane splitting process and propose a model for the estimation of CO₂. The model calculates the emissions flow rates from furnaces, boilers and integrated gas turbines. According to the authors the CO₂ emission can be decreased by 83% using internally heat-integrated distillation column compared to conventional alternatives in the case of a state of art propylene-propane split. In my thesis the CO₂ emission calculations are verified using the model proposed by Gadalla et al²⁴.

These studies, however, do not make a complex investigation of the different energy consuming systems and their environmental effects, that is, how the results of the exergy analysis can be applied to evaluate economic and environmental features in advance making the process design step simpler. Therefore, the goal of my study is to elaborate and propose such an evaluation methodology of process design alternatives that helps to accomplish more energy efficient, economic, and environmental friendly processes. The proposed methodology is evaluated and demonstrated on energy-integrated distillation systems and helps to decide among the different kinds of energy integration solution for ternary mixture separation.

The final aim is to classify the different process design alternatives to make the evaluation of the synthesis step simpler at the early stage of process design.

2.5 Controllability issues and dynamic behaviour

The chemical processes during their operation must satisfy several requirements imposed by the designers such as production specifications, operational constraints, economics, environmental regulations. These requirements dictate the need for control structures, which realize the continuous monitoring of the operation. The task of the control structure usually is to suppress the influence of external disturbances, to ensure the stability of the chemical process, and to optimize the performance of the chemical process.

Unit operations like distillation are generally controlled with feedback control loops. The main elements of these feedback control loops are the output, potential disturbance, and available manipulated variable. The disturbance changes unpredictably and according to the control objective, the output has to be kept at the desired value. The feedback control works as it follows (**Figure 1**): the sensor measures the value of output that is compared with the desired value (set point) and the deviation is supplied to the controller. The controller changes the value of the manipulated variable in order to reduce the magnitude of the deviation. Usually, the controller affects the manipulated variable through the final control element (e.g. control valve).

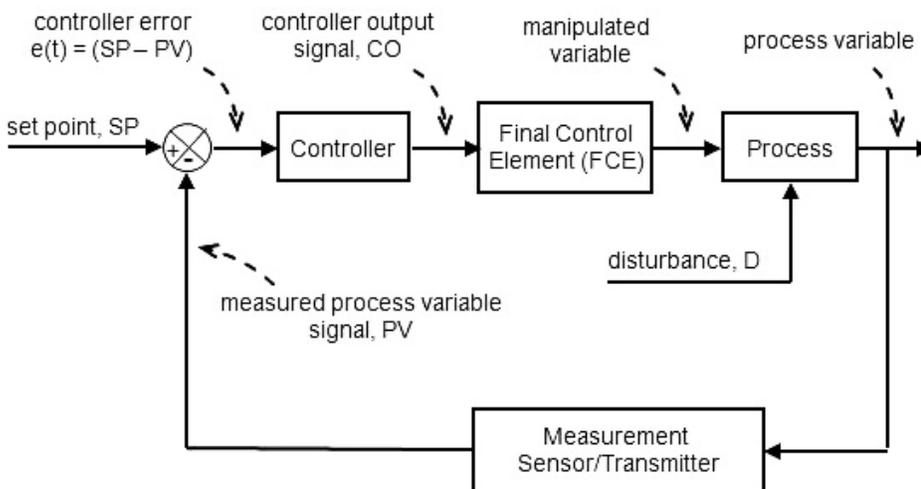


Figure 1 General feedback control loop block diagram.

The binary distillation column shown in **Figure 2** has two degrees of freedom which can be used to specify top and bottom compositions. Apart from the compositions, the levels and pressures may vary from the control point, so the distillation column may be viewed as a 5×5 system²⁵. The 5 manipulated variables are: reflux rate (L), distillation rate (D), bottom rate (B), heat duty of the reboiler (Q), column head vapour rate (V), and / or their ratio. The controlled variables are: levels in top and bottom, top and bottom composition, and column pressure.

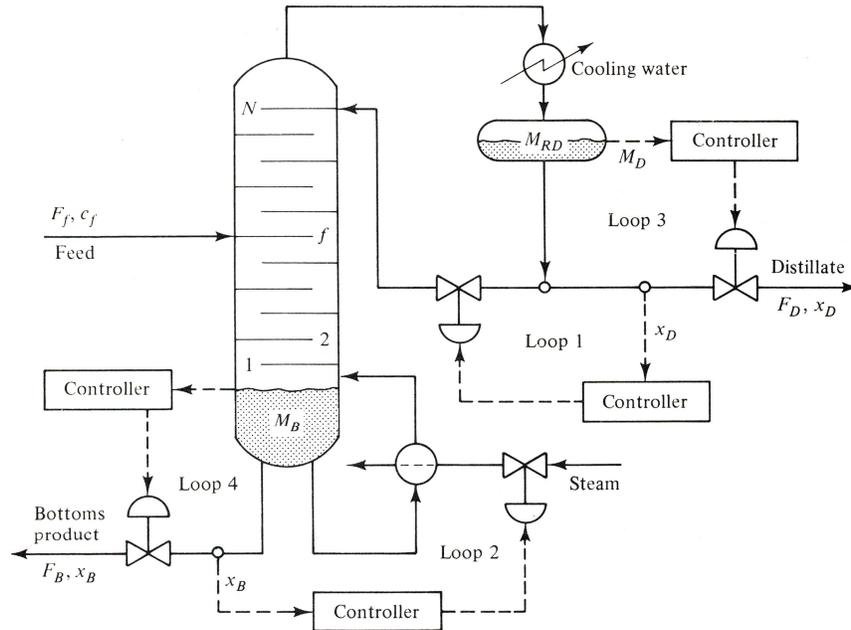


Figure 2 Binary distillation column with control loops²⁵.

The process design procedure is a sequential discipline, where the control design is carried out after the plant is designed. During plant design a number of basic plant performance requirements have to be ensured in order to obtain a design which provides acceptable operational performance. Usually, the process design alternatives are judged on economic aspects alone without taking operability into account.

Operability is the ability of the plant to provide acceptable static and dynamic operational performance that includes flexibility, switchability, controllability and several other issues²⁶.

The switchability measures the ease of moving the process from one desired stationary point to another. Similarly, resiliency measures the degree to which a processing system can meet its design objectives despite external disturbances and uncertainties in design parameters.

Controllability is a capability of a process to operate economically and safely, without violating constraints, achieving various design objectives in the presence of these uncertainties. Since controllability is an inherent property of the process itself, it should be considered at the design stage before the control system design is fixed. The most preferable way to consider controllability at the design stage is to include controllability as one of the design objectives just like traditional economic ones in the design optimization problem.

Controllability evaluation methods may be classified into three types by the model used in the evaluation procedure, steady-state model-based, linear dynamic model based, and nonlinear dynamic model-based ones. Another way to evaluate controllability quantitatively and explicitly is performing dynamic simulations of the target process. However, detailed dynamic simulation requires detailed information on the system, which is not known until the later part of design stage. Hence, in the last decades different authors²⁷⁻³¹ have developed simple controllability study methods, which can be carried out in the early design phase.

In addition, it is important to emphasize that the controllability analysis usually is applied for two type of problem:

- i. Selection of the best controlled and manipulated variable pairing within one process^{32, 33}.
- ii. Evaluation of control properties for two or more process alternatives^{34, 35}

The controllability analysis is carried out by calculating the transfer function matrices (G) with the CDI interface of the Aspen Dynamics. These transfer function matrices are subjected to SVD (Singular Value Decomposition):

$$G = U\Sigma V^H \quad (5)$$

where the G is an $l \times m$ matrix, Σ is an $l \times m$ matrix with , $k = \min (l, m)$ non-negative singular values, σ_i , arranged in descending order along its main diagonal; the other entries are zero. U is an $l \times l$ unitary matrix of output singular vectors, u_i , V is an $m \times m$ unitary

matrix of input singular vectors v_i and H denotes the complex conjugate transpose of the corresponding matrix³⁶.

In order to carry out the controllability study, different control indices were elaborated, which are used to predict the degree of directionality and the level of interactions in the system. These indices can be calculated in steady state or in frequency domain. The controllability indices applied in my thesis are the following.

2.5.1 Condition number (CN)

CN of the transfer function matrix is the ratio between the maximum and minimum singular values:

$$\gamma(G) = \frac{\bar{\sigma}(G)}{\underline{\sigma}(G)} \quad (6)$$

where $\bar{\sigma}(G)$ is the maximum singular value and $\underline{\sigma}(G)$ the minimum singular value of the transfer function matrix. CN, lower than 10, indicates a well controllable process³⁶. A matrix with condition number larger than 10^3 is said to be ill-conditioned which implies that the system is sensitive to unstructured input uncertainty. Theoretically, if the CN is smaller than 10 the effects of the input uncertainty are always negligible. In contrast, the large CN indicates the model sensitivity in general, but it does not hold in every case. Therefore, the control structure with large CN can not be excluded from the possible ones.

2.5.2 Morari resiliency index (MRI)

MRI also named as minimal singular value of the open-loop transfer function, which stands for a specific input and output direction. The control system that presents large value for MRI is preferred. Large MRI values indicate that the process can handle disturbances without saturation of the manipulated variables²⁷.

2.5.3 Relative Gain Array Number (RGAno)

RGAno is calculated from the relative gain array (RGA) which is the square matrix defined as:

$$RGA(G) = G \times (G)^{-T} \quad (7)$$

where \times is the Hadamard product and T denotes the transpose of the corresponding matrix.

In the work of Bristol³⁷ the RGA is proposed as a tool for pairing controlled and manipulated variables in decentralized control system. Variable pairings corresponding to positive relative gains should be preferred as close to unity as possible. Negative gains or relative gains much larger than unity should be avoided, and large negative relative gains are particularly undesirable.

RGA indicates the preferable variable pairings in a decentralized control system based on interaction considerations and also provides information about integral controllability, integrity, and robustness with respect to modelling errors and input uncertainty²⁸. The RGA_{no} defined in equation 8 shows the deviation of the RGA from unity:

$$RGA_{no} = \|RGA(G) - I\|_{sum} \quad (8)$$

However, the controllability study based on different control indices is a promising evaluation method for selection of the best controlled and manipulated variable pairing; many authors do not support its application without load rejection analysis in time domain because the latter one entirely reveals the dynamic behaviour of the distillation systems.

Gross et al³³ describes a controllability analysis of an industrial heat-integrated distillation process. The purpose of the work is to select the best controlled and manipulated variable pairing for the studied heat-integrated distillation system. In order to reveal the control properties of the system the authors carry out steady state controllability analysis calculating RGA, Niederlinski index, MRI, CN. The steady state controllability analysis is followed by dynamic controllability analysis where the control indices are calculated in frequency domain. The results of the controllability analysis are verified by a load rejection analysis, in other words by analyzing the closed-loop behaviour of the distillation systems. The authors find that the controllability analysis can only offer some hints about the dynamic process behaviour. This emphasizes the point that a controllability analysis should be rather seen as a necessary than a sufficient condition for selecting manipulated variable alternatives in the process design.

Based on the controllability study alone it is very difficult to decide which control structure alternative is the best and which is the second best.

Haggblom²⁸ proves that the frequency dependent RGA is suitable for evaluation of distillation control structures only by considering the partially controlled plant obtained by closing the inventory control loops.

Other authors like Lee et al³⁸ consider that the relative gain array cannot be effectively applied to dynamic systems for controllability evaluation however it is widely used as a controllability index of steady-state systems.

Based on the publications in the literature can be concluded that the controllability study used for controlled and manipulated variable pairing selection within a distillation system is not reliable and the results should be verified by closed loop simulations. In the case when the authors^{34, 35} evaluate the control properties of different distillation system alternatives the applied controllability study can predict which alternative is easier to control.

Bildea et al³⁴ presents a comparative study of sloppy distillation system with forward heat-integration (SQF) and with backward heat-integration. The aim of this work is to prove the relationship between the design and control of the distillation systems. The applied tools are the frequency dependent controllability analysis and the closed-loop simulation. The authors find that the two investigated distillation systems have similar energy consumption but their dynamic behaviour differs. The controllability analysis predicts - in all situations - better dynamic properties for the sloppy distillation system with forward heat-integration.

Gabor et al³⁵ presents a simple methodology for the determination of controllability indices in the frequency domain. The authors apply this methodology on two different thermally coupled distillation systems (side-stream stripper and side-stream rectifier) and investigate the controllability and dynamic behaviour of these. The controllability investigation is applied both for selection of the best controlled and manipulated variable pairing within one distillation system and for control properties comparison of two distillation system alternatives. However, the selection of controlled and manipulated variable pairing is based on controllability indices the results are not tested with the more reliable closed loop simulation. Thus, the paper do not prove that the frequency

dependent controllability indices can select the best control structure for a given distillation system. Conversely, in the following part of the paper the two thermally coupled distillation systems are evaluated with the frequency dependent controllability indices and closed loop simulation as well. The authors find that the results of the frequency dependent controllability indices and closed loop simulation are in correspondence and the comparative study can select the distillation system with better control properties in the case of different ternary mixtures.

Mizsey et al³⁹ investigate the control properties of three different energy-integrated distillation systems, namely the direct distillation sequence with backward heat integration (DQB), with forward heat integration (DQF), and fully thermally coupled distillation column (FTCDC). Their controllability study is based on the degrees of freedom analysis and the steady state analysis tools for both energy-integrated schemes. First, the controlled and manipulated variables are selected on the basis of engineering judgment, secondly, the possible pairings of these controlled and manipulated variables for composition control loops are analyzed by steady state tools to determine the most promising candidates of the control structure, and finally, dynamic simulations are carried out for all energy-integrated schemes with the previously selected control structure candidates to determine the best of them. This work selects the promising control structures based on the steady state controllability indices and the selection is verified by closed loop simulations in time domain. The control properties of the energy-integrated distillation systems are compared between each other and the authors conclude that the FTCDC is less favourable than the heat-integrated distillation schemes.

None of the papers mentioned above on controllability evaluation topic try to aggregate the different control indices. On the contrary these indices are considered individually. However, they may show opposite operability characteristics for a given control structure. Often the results of the controllability studies are difficult to interpret because of the controversial index results for a given control structure (e.g. the value of the CN is close to the desirable domain but the RGA value indicates strong interactions).

Chapter 3 The investigated case studies

3.1 The studied energy-integrated distillation systems

Three type of energy-integrated distillation systems are studied and are compared to the conventional scheme. In case of ternary mixture separation, distillation systems consist of two columns. In this thesis direct separation sequence is analyzed. The studied distillation systems are selected from different types of conventional and energy-integrated distillation groups. The best connection is chosen from this groups referring to the column coupling and to the direction of energy integration. First distillation system is a direct sequence with backward heat integration instead of forward because of its better economic and control features highlighted by Rév et al⁴⁰. The sloppy distillation structures with forward and the backward heat integration have similar characteristics in energetic point of view. The forward heat integration is chosen for my study because of its better control properties demonstrated by Bildea et al³⁴ and Emtir⁴¹.

The studied distillation systems are the followings:

3.1.1 Direct sequence with backward heat integration (DQB).

In the case of the separation of ternary mixtures, the heat-integrated distillation system consists of two columns. The direct separation sequence with backward heat integration is studied. The base idea of this distillation system is to use the overhead vapour from the second high-pressure column to provide heat to the first low-pressure column. The reboiler of the first column is combined with the condenser of the second (**Figure 3**).

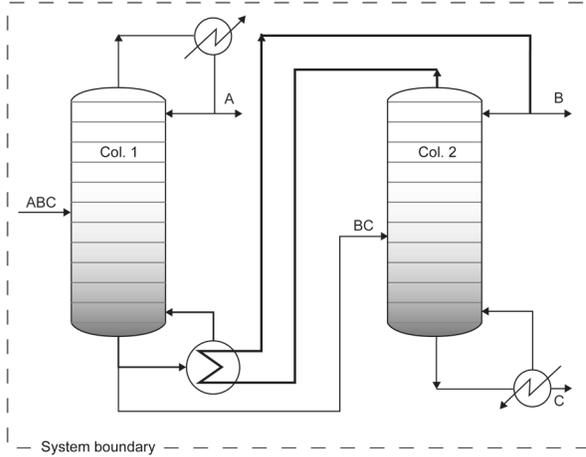


Figure 3 Direct distillation sequence with backward heat integration (DQB).

3.1.2 Fully thermally coupled distillation column (FTCDC).

Fully thermally coupled distillation column is also called Petlyuk column consists of a prefractionator and a main column. The required heat amount for the separation is provided through direct contact of the material flows (Figure 4). In the prefractionator it is required to have the most volatile component (A) of the ternary mixture only in the top product, and to have the heaviest component (C) only in bottom product. The middle component (B) distributes between the top and bottom products. The top product ($V_{12} - L_{21}$) and the bottom product ($L_{12} - V_{21}$) can be estimated ¹¹.

The top product of the prefractionator can be calculated with equation 9:

$$V_{12} - L_{21} = A + \beta B \quad (9)$$

The bottom product of the prefractionator can be calculated with equation 10:

$$L_{12} - V_{21} = C + (1-\beta) B \quad (10)$$

The optimal fractional recovery of the middle component estimates the flow rates in the prefractionator where the energy consumption of the FTCDC is minimal:

$$\beta = \frac{\alpha_B - \alpha_C}{\alpha_A - \alpha_C} \quad (11)$$

where β is the optimal fractional recovery of the middle component and it had been defined by Treybal ⁴²; α_i is the volatility of component i .

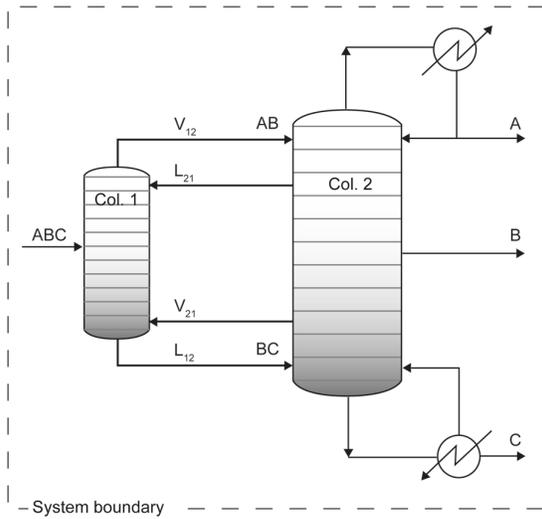


Figure 4 Fully thermally coupled distillation column (FTCDC).

3.1.3 Sloppy distillation system with forward heat integration (SQF).

This distillation system basically is a heat-integrated sequence, but in the prefractionator sloppy separation takes place. The middle component distribution in the prefractionator is similar to the Petlyuk column. There is no material flow from the main column to the prefractionator. The first column is a high pressure prefractionator, its distillate and bottom product are fed to the second, low-pressure column. The forward heat integration between the two columns is carried out by an integrated heat exchanger, where the overhead vapour from the high-pressure prefractionator is used to boil up the low-pressure column (**Figure 5**). The forward scheme was selected in this work because previous studies^{34, 41} have shown that it is better controllable than the backward integration.

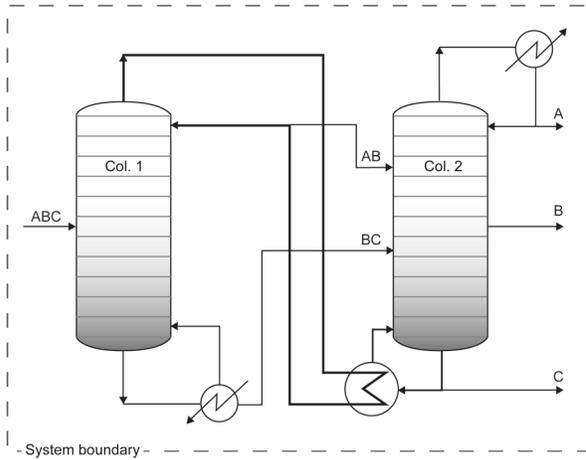


Figure 5 Sloppy distillation system with forward heat-integration (SQF).

3.1.4 Conventional direct distillation scheme (Conv. Dir.) is used as base case for comparison. It consists of two simple distillation columns connected in such a way that bottom product of the first column is the feed of the second column. In literature, they are considered to be conventional arrangements for ternary distillation. Direct separation sequence is studied (Figure 6).

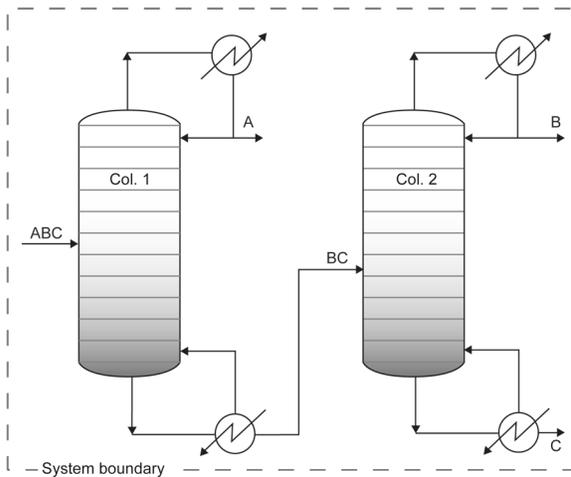


Figure 6 Conventional direct distillation scheme (Conv. Dir.).

3.2 Separation tasks

For the overall investigation of the distillation systems, three different ternary mixtures are selected (**Table 1**).

Three product purities are supposed in the economic study (Table 2).

Table 1 Ternary mixtures studied

Case	Mixture	α_A	α_B	α_{AB}	β	SI
1	isopentane-pentane-hexane	3.62	2.78	1.3	0.68	0.47
2	pentane-hexane-heptane	7.38	2.67	2.76	0.26	1.03
3	butane-isopentane-pentane	2.95	1.3	2.26	0.154	1.74

Table 2 Expected product purities

Case	Product Purities (%)
1	99
2	95
3	90

The chosen ternary mixtures have different ease of separation that can be characterized by the separation index (SI), presented in equation 3.

The results of this work are often presented as a function of SI which gives indication about the location of the more difficult separation task.

In mixture 1 *A/B* separation is more difficult than *B/C* separation ($SI < 1$). In mixture 2 *A/B* separation is as difficult as *B/C* separation ($SI \sim 1$), the ease of separation is balanced. In mixture 3 the *B/C* separation is more difficult than *A/B* separation ($SI > 1$).

The heat-integrated distillation system with backward heat integration (DQB) is also investigated for the separation of 14.1 % N,N-dimethylformamid (DMF) containing aqueous solution through an industrial case study of retrofit design. The separation task in this case study is presented in **Table 3**.

Table 3 Separation task for DQB industrial case study.

Feed mixture content	Feed mixture composition (%)	Product Purities (%)
DMF	14.1	95
Water	85.9	99.9

Chapter 4 The proposed complex evaluation methodology

4.1 Introduction

In the course of process design there are several steps on different design layers of the process synthesis activity⁴³. These general steps of a process design project are: conceptual design, detailed engineering design, project execution, start up and trial runs, and finally the production. In the conceptual design step also known as early stage of the process design complex evaluation can be carried out since the process design became computer aided in the last decades and does not require as much time and effort as in the past. There are also several attempts to make the process synthesis activity simpler so that the design engineer can find the best process alternative. In this early phase of design, the conception of elaboration methodology has a great importance.

4.2 Definition of the evaluation methodology

My work proposes an evaluation methodology of distillation systems that consists of three levels and takes into account exergy, economic, and emission criteria in order to find the most adequate process structure.

These three levels of the methodology are the following:

- 1.) definition of the problem and selection of the competitive process alternatives
- 2.) multicriteria evaluation of the process alternatives including exergy analysis, economic study, and GHG emission estimation.
- 3.) ranking of the process alternatives based on the summarized indicator and the choice of the most adequate one.

The proposed methodology is demonstrated on distillation systems as one of the highest energy utilising system in the separation industry. The steps of the methodology are shown in **Figure 7** and are described as follows.

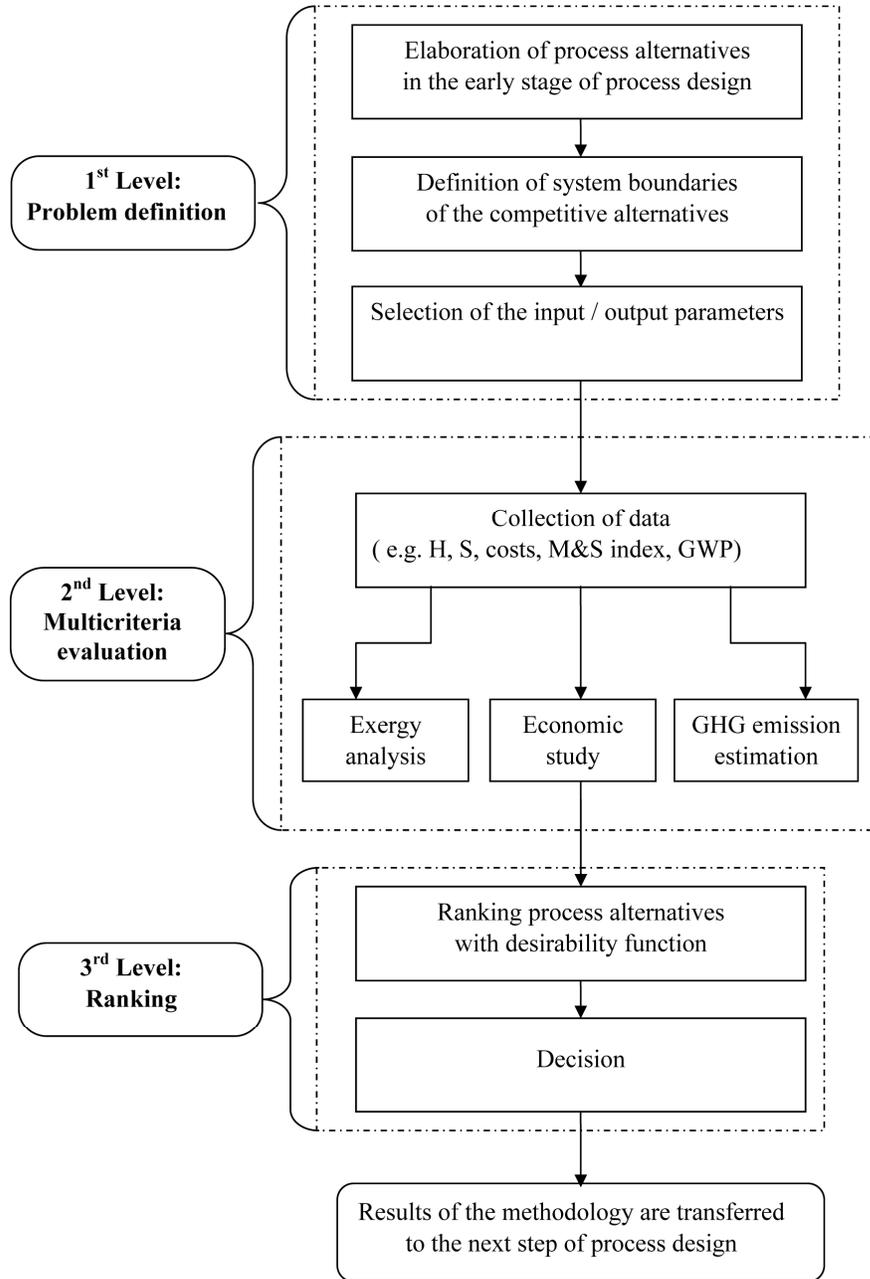


Figure 7 Flow diagram of the complex evaluation methodology of distillation systems.

4.3. The first level of the methodology

The first level of the methodology named as the problem definition includes the elaboration of process alternatives, the definition of system boundaries, and the selection of the input / output parameters.

4.3.1 The elaboration of the process alternatives

The elaboration of the process alternatives in the case of the distillation processes consists of the preliminary shortcut design defining the number of trays, feed location according to the separation task. The set of the process alternatives increases with the consideration of the available energy integration, which can have different types and can be used at different locations. This step also includes the selection of the competitive design alternatives from the wide range of solutions.

4.3.2 Definition of system boundaries

The second step of the methodology defines the system boundaries of the competitive alternatives. The well-defined process segments include the distillation columns and the process utilities in this work and they are subject to the comparative study.

4.3.3 Selection of input / output parameters

The selection of identical input/output parameters makes possible the comparative study of the distillation design alternatives. The basic assumption is the fixation of the input and output data in order to study the process itself, thus the different distillation design alternatives can be compared between each other or to a reference process.

4.4 The second level of the methodology

The second level of the methodology carries out the multicriteria evaluation of the design alternatives.

4.4.1 Collection of the necessary data

The starting step is the collection of data necessary for the different analyses. The summary of the data is presented in **Table 4**.

Table 4 Summary of the data required for the application of the evaluation methodology

Analysis	Data
Exergy	Ambient pressure Ambient temperature

	Molar enthalpy of component i
	Molar entropy of component i
	Relative volatility of components ij
Economic	Cost of the utilities
	Heat capacity
	Latent evaporation heat
	Marshall & Swift index
	Material costs
Greenhouse Gas	Global warming potential of component i
Emission Estimation	Efficiency of the firing equipment

The multicriteria evaluation of distillation system alternatives focuses on (i) exergy analysis, (ii) economic study, (iii) GHG emission estimation. Each of the analysis calculates an indicator that can be summarized at the next level of the evaluation methodology. These indicators are the following: thermodynamic efficiency, total annual cost, and the carbon dioxide equivalent emission. The following section describes the applied analyses in detail.

4.4.2 Exergy analysis

Energy efficiency of the studied process alternatives can be calculated based on the first law of thermodynamics, which leads to an energy analysis. Since not all the heat energy can be converted to useful work, stated by the second law of thermodynamics, exergy analysis proves to be more adequate to determine the thermodynamic efficiency of the process alternatives. By definition, exergy is the maximum capacity of the system to perform useful work as it proceeds to a specific final state in equilibrium with its surroundings.

In the case of distillation systems, the columns can be considered as heat engines and their exergy demand is the minimum isothermal work of separation. Instead of mechanical work, separation work is produced. The purpose of this analysis is to compare the energy saving performance of the evaluated distillation systems based on thermodynamic efficiency, which gives information about the efficiency of the supplied

heat conversion into separation work in the distillation systems. Apart from the thermodynamic efficiency, the exergy loss is also calculated that shows the energy wastes. The distillation design alternatives have good potential for improvement regarding energy saving when it has considerable exergy losses and low thermodynamic efficiencies¹⁸. The thermodynamic efficiency is selected as indicator in the evaluation methodology and it can be calculated⁴⁴ with the following equation 12:

$$\eta = \frac{W_{SEP}}{Ex_{loss} + W_{SEP}} \quad (12)$$

where W_{SEP} [kW] is the work of separation, Ex_{loss} [kW] is the exergy loss of the system.

The separation work can be defined with the equation 13.

$$W_{SEP} = \sum_{outlet} nEx - \sum_{inlet} nEx \quad (13)$$

where n [kmol/h] is the mole flow of the inlet and outlet streams, the Ex [kJ/kmol] is the specific exergy which can be calculated with the equation 14.

$$Ex = H - T_0 S \quad (14)$$

where H [kJ/kmol] is the molar enthalpy, S [kJ/kmol K] is the molar entropy and T_0 [K] is the ambient temperature which is fixed at 283 K in this work.

Gouy-Stodola theorem^{45, 46} states that the lost available work is directly proportional to the entropy production. The proportionality factor is simply the ambient temperature T_0 :

$$Ex_{loss} = T_0 \Delta S_{irr} \quad (15)$$

Based on the second law of thermodynamics the entropy production can be calculated:

$$\Delta S_{irr} = \sum_{outlet} (nS + \frac{Q_{cond}}{T_{cond}}) + \sum_{inlet} (nS + \frac{Q_{reb}}{T_{reb}}) \quad (16)$$

where Q_{cond} and Q_{reb} [kW] are the heat duties of the condenser and reboiler, T_{cond} and T_{reb} [K] are the temperatures of the cooling and heating media, respectively.

However, the exergy analysis calculates also the exergy loss, only the thermodynamic efficiency is selected as indicator in the evaluation methodology. The reason behind this selection is that the exergy loss profile can provide information about the location of the

energy wastes within the distillation system while the thermodynamic efficiency characterizes the complete process segment. The exergy loss and thermodynamic efficiency together provide useful information e.g. in the case of retrofit design because they indicate the possibility of further energy savings for a specific distillation system.

4.4.3 Economic Study

Economic features should be estimated throughout every stage of the process design. The purpose of the economic study is the determination of the economic efficiency in function of their capital and utility costs. The correlation between economic study and exergy analysis is important as well, because e.g. exergy analysis may give hints about economic properties of the system. In order to compare these results with that of the exergy analysis the same operating conditions are used. Thus, the separation tasks and the inlet / outlet stream properties are identical to the parameters used during the exergy analysis. The objective function is the Total Annual Cost (TAC) that includes capital and utility costs and it is calculated according to the equation 17.

$$TAC = \text{Annual capital cost} + \text{Annual operating cost} \quad (17)$$

$$\text{Annual capital cost} = \text{Capital cost} / \text{Plant life time} \quad (18)$$

The operating cost includes the utility costs and it is calculated per year as a function of the operating hours. Marshall and Swift cost index is used to update the capital costs to the present time of the estimate. It takes in account the inflation and other factors, which contribute to the change of the equipment prices. This cost index is recommended for use with process-equipment estimates and chemical-plant investment estimates. The economic study provides the TAC as indicator that characterizes the different distillation design alternatives.

4.4.4 Greenhouse gas emission estimation

As the environmental emissions regulations have grown stricter in the last decades, the GHG emission estimation has especial importance and it should be included in the early stage of process design. This work considers only the GHG emission since this form the most significant part of the pollution caused by the studied distillation processes. The emission inventory and quantification motivates the designer to realize environmental

friendly processes. These emissions have also special impact on the profitability of industrial processes since the Kyoto Protocol was ratified by many countries and it was established a scheme for GHG emission trading in 2005. Some countries have introduced taxes based on the carbon content of the energy products and this tax is called ‘carbon tax’. A ‘carbon tax’ is a charge to be paid on each fossil fuel, proportional to the quantity of carbon emitted when it is burned. Concerning the present demands, carbon dioxide equivalent emissions need to be quantified.

Estimation of carbon dioxide equivalent (CO₂e) emission: beside of CO₂ emission other greenhouse gases are also estimated like nitrous oxide (N₂O), methane (CH₄), hydrofluorocarbons, and sulfur hexafluoride (SF₆) (Table 5).

Table 5 Global warming potentials of different greenhouse gases

Greenhouse Gases	GWP value/100 years
Nitrous oxide (N ₂ O)	296
Methane (CH ₄)	23
Trifluoromethane (HFC-23)	12000
1,1,1,2-Tetrafluoroethane (HFC-134a)	1300
Sulfur hexafluoride (SF ₆)	22200

The CO₂e is calculated by summing up the GHG emissions multiplied by their GWP value (eq 19).

$$CO_2 \text{ equivalent emission} = \sum (GWP \times \text{Greenhouse gas emission}) \quad (19)$$

The GHG emission estimation calculates the CO₂e emission of the distillation design alternatives per year that can be used as indicator in the evaluation methodology.

4.5 The third level of the methodology

The third level of the methodology includes the ranking of the process alternatives and the decision which system is the most adequate for the specific task.

4.5.1 Ranking process alternatives based on desirability function

The ranking is based on the desirability function, where the input data are the indicators calculated on the previous level. The indicators provide important information about process performances and allow the comparison of process alternatives with respect to specific aspects. However, they are not suitable for a direct comparison among the different analyses; therefore, the desirability function (D_{fct}) is used to summarize the different indicators. The D_{fct} is selected among the other methods, which can be found in the literature because different criteria with different engineering units can be aggregated in one process indicator and nonlinear functions can be used in the optimization procedure.

The desirability function (D_{fct}) approach is a useful statistical method to optimize the multiple characteristics problems. This method proposed by Harrington⁴⁷ converts the multiple quality characteristics into a single characteristic problem by maximizing the total desirability. The indicators are transformed into an individual desirability value d for the desirability function model. If the response exceeds the acceptable value, the value of d becomes 0; if the response is at the target value, the desirability value d becomes 1. The individual desirability functions, d are continuous functions and they are chosen from among a family of linear or exponential functions. Based on these individual functions the overall desirability function, D_{fct} , is constructed (eq 20), and this makes possible the ranking of the process alternatives. The D_{fct} is defined as the geometric average of the k individual desirability functions and desirability includes the designer priorities and desires using the m weight factor⁴⁸.

$$D_{fct} = \left(\prod_{i=1}^k d_i^{m_i} \right)^{\frac{1}{\sum m_i}} = \left(d_1^{m_1} \times d_2^{m_2} \times \dots \times d_k^{m_k} \right)^{\frac{1}{\sum m_i}} \quad (20)$$

where k is the number of indicators and m is the weight factor.

High value of D_{fct} shows that all d_k are toward the target value that indicates the most adequate process alternative.

The form of the d_k functions are selected in such a manner that describes the nature of the criterion that should be maximised or minimised (equations 20a, 20b and 20c). The constant in the power in the exponential d_k function has the same engineering unit as the numerator.

$$d_1 = 1 - \exp(-\text{Therm.Effic.}/10) \quad (20a)$$

$$d_2 = \exp(-\text{TAC}/10) \quad (20b)$$

$$d_3 = \exp(-\text{CO}_2\text{e}/10) \quad (20c)$$

4.5.2 Decision

The last step of the methodology is the decision making based on the D_{fct} . The process alternative with the highest D_{fct} value is the most favourable solution for the specific separation task based on the criteria mentioned in the second level of the evaluation methodology. The selected process alternative can be subject to the detailed engineering design as the next step of the process design project.

4.6 Application of the proposed evaluation methodology on the studied distillation systems

Optimal parameters of the above mentioned separation systems are determined. Rigorous tools calculate adequate reflux ratios, number of trays, and optimal feed tray. In the case studies selected, the total number of the theoretical trays of the separation schemes ranges between 70-95 and the column diameters range between 0.9-1.5 m. The reflux ratios vary according to the ease of separation in a wide range. The simulation models of the studied distillation systems are implemented in the ASPEN PLUS process simulator. The exergy analysis and economic study require the use of MS-Excel connected to the process simulator where the different exergy calculating equations or the cost functions are introduced.

Definition of the boundaries

The methodology is applied on the process segment that contains the distillation columns and the heat exchangers, including the condensers and reboilers.

Selection of the input / output parameters

For the investigation of the distillation systems, three different ternary mixtures are selected (Table 1). Mixtures of more than three components are not considered at the stage of this study so that the complexity of the several designs, that is typical for the more than three component mixtures, does not disturb the overview of my proposed

methodology. Because of the same reason, only zeotropic mixtures are considered. Three product purities are supposed in the economic study (

Table 2).

In the case of the exergy analysis and GHG emission estimation one product purity (95%) is selected. Feed flow rate is 100 kmol/h and its composition is always equimolar. The Soave-Redlich-Kwong model is used to calculate vapour-liquid equilibrium. This model is widely used in the refinery and gas processing industries for the prediction of vapour-liquid equilibria for systems containing non-polar components.

The ambient pressure and temperature is taken 101 kPa and 298 K respectively.

Results of the exergy analysis

Exergy analysis is applied to the studied energy-integrated distillation systems and to the conventional direct distillation scheme.

In order to perform the exergy analysis the balance regions has to be fixed. Figure 3-5 show the system boundaries where the exergy analysis is applied. The analysis takes into account the inlet and outlet material streams and the heat duty of the reboilers and of the condensers. In order to compare the thermodynamic efficiency of the studied distillation systems the entering and leaving stream physical properties must be identical. In this study the temperature, pressure, and composition of the inlet and outlet streams are equal for each case study and the product purity of the outlet streams is selected to be 95%. Therefore, the inlet and outlet stream exergies are identical for the studied distillation systems separating one specific ternary mixture. Thus, the separation work does not vary as a function of the used distillation system only in function of the separated mixture. The cooling water temperature is taken 283 K and the temperature of the steam used in the reboilers is 433 K. The calculated thermodynamic efficiency (eq 12) is linear dependent on the taken temperature grades ⁴⁹ thus one can obtain different efficiency values if the temperature of the used cooling and heating media is different or the ambient temperature is fixed differently.

Each distillation system is studied for three different ternary mixtures (**Table 1**) in order to investigate also the effect of SI on the energy saving properties of the distillation systems. The distillation systems are ranked according to their exergy loss and thermodynamic efficiency.

In Figure 8 the exergy loss is presented as a function of SI for each distillation system. The three SI value represents the three ternary mixtures with different ease of separation. As the figure shows the exergy loss is the lowest when the ease of separation of the mixture is balanced so the SI value is close to 1. If the ease of separation becomes unbalanced thus the SI of the mixture differs from 1 the exergy loss increases. Generally, the exergy loss of the distillation systems is the highest in the case of the third mixture separation with SI=1.74. It has to be noted that SI value of the third mixture deviates the most from 1 which means that this mixture is the furthest from the symmetric ease of separation.

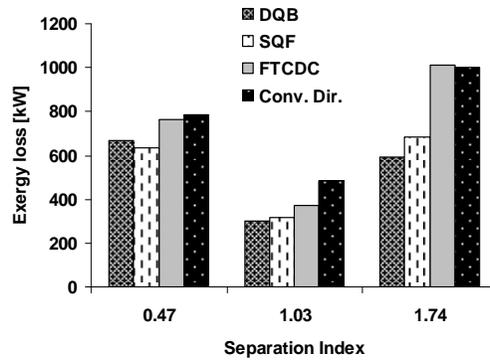


Figure 8 Exergy loss in function of the separation index.

The comparison of the different distillation systems shows that the DQB has the smallest exergy loss followed by SQF. Entirely, these two heat-integrated distillation systems show the best energy saving alternatives and consequently the thermodynamic efficiency of these systems is the highest (Figure 9).

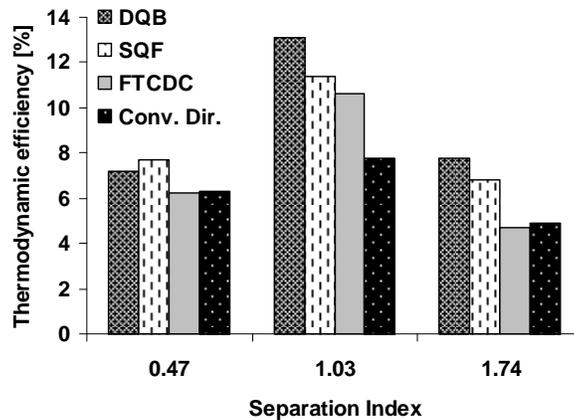


Figure 9 Thermodynamic efficiency in function of the separation index.

The thermodynamic efficiency of the FTCDC is better compared to the conventional direct scheme in the case of the mixtures with $SI=1.03$ and in the case of the other mixtures there is a very slight difference in the thermodynamic efficiency of the FTCDC and conventional direct scheme. **Figure 9** shows that the DQB has 5% higher thermodynamic efficiency than that of the conventional direct scheme in the case of mixture 2 with $SI=1.03$. These results support the idea that processes with high exergy loss and low thermodynamic efficiency can be energetically improved¹⁸.

In order to localize the exergy loss in the distillation system, the exergy analysis can be applied separately on the process units. **Figure 10** shows the quantity of the exergy loss of the two distillation columns. The exergy loss in the prefractionator (column 1) of the FTCDC is low since it has neither reboiler nor condenser.

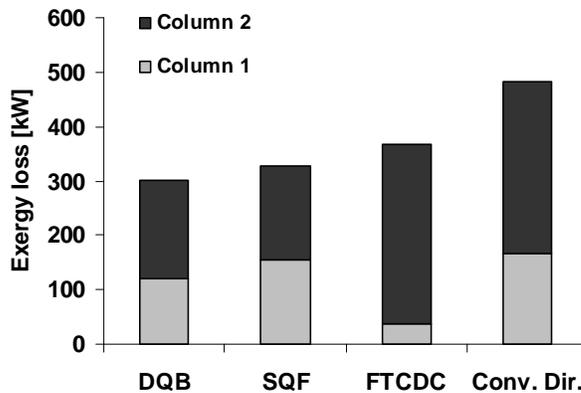


Figure 10 Exergy loss of the two distillation columns in the case of mixture with $SI=1.03$.

The results of the exergy analysis are compared to the energy consumption data of the distillation systems. The calculation of the energy consumption assumes that the distillation systems have only heat requirements neglecting e.g. the electricity usage of the pumps etc. The heat demand of the studied distillation systems is presented in the Figure 11. One can notice that the tendency of the heat demand is similar to that of the exergy analysis. This can be explained with the identical ambient and utility temperatures for each case study.

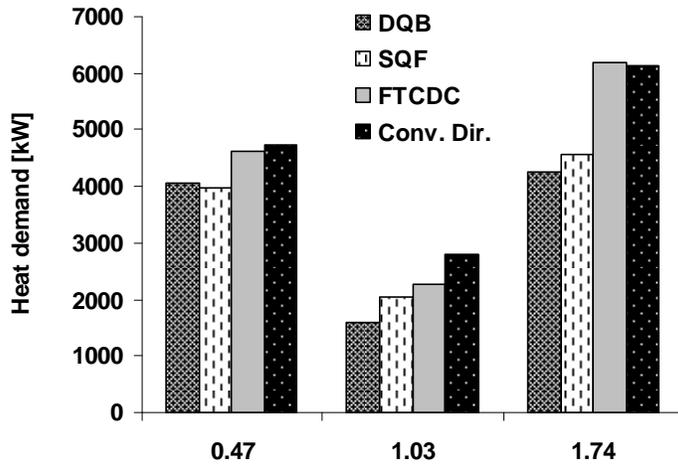


Figure 11 Heat demand of the distillation systems in function of the separation index.

The exergy analysis determines the thermodynamic efficiency of the investigated systems which gives information about the supplied heat conversion into separation work and identifies the energy wastes through the exergy loss. This tool reveals the energy saving performance of the system and locates those process units which need further energetic improvements.

In the case study the exergy analysis identifies the characteristics of the studied distillation systems regarding to the energy efficiency but it is uncertain how precisely the costs or the CO₂e emission of these systems can be predicted. Therefore the next steps of this work are an economic study calculating the costs of the studied distillation systems and furthermore the estimation of the CO₂e emission.

Results of economic study

The economic study as a design step is tested on the distillation design alternatives. Based on their economic efficiency the investigated distillation schemes are compared between each other and the best energy integration solution can be chosen. The economic study calculates the TAC of the investigated distillation systems. These systems are investigated for the same separation task and within the same system boundaries as in the exergy analysis. The TAC is calculated in the function of the separation index. In the literature, economic feature of energy-integrated distillation schemes have been discussed with increase of product purity^{11, 40}. However, it has not been investigated in the aspect

of separation index, which expresses the ease of separation of the given mixture. The SI allows the generalization of the ternary mixtures based on their relative volatility.

Concerning the TAC (eq 17, 18) calculation in this case study, the plant life time is 10 years with 8000 operating hours per year. The capital cost contains the installed cost of the column shell, tower internals, condenser and reboiler. These costs are estimated using respective equations proposed by Douglas⁴³ and updated by the Marshall and Swift index which value is taken from literature⁵⁰. Operating cost contains the cooling water and steam costs. The industrial prices are used to calculate the utility costs. The equations used for capital and operating cost calculations are presented in the Appendix A.

Results of the comparative economic study for the separation systems and ternary mixtures studied are shown in **Figure 12-11**. The representation of the results in these three figures differs in the expected product purities. The effect of different product purity requirements is investigated in order to reveal the properties of the investigated distillation system alternatives in detail.

Figure 12 shows the Total Annual Cost (TAC) vs. Separation Index (SI) when the required product purity is 90%. In this case the most economic distillation structure is the direct sequence with backward heat-integration (DQB) followed by the sloppy distillation system with forward heat integration (SQF). Fully thermally coupled distillation columns show savings compared to the conventional direct distillation scheme which has the highest costs.

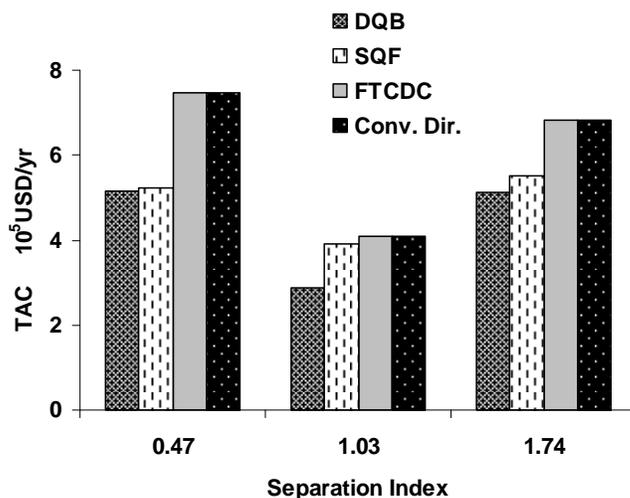


Figure 12 TAC vs. SI when the required product purity is 90%.

In the next case where the required product purity is 95% (**Figure 13**) total annual cost of each distillation structure increase and the rank between of the heat-integrated distillation systems (DQB, SQF) does not change. The FTCDC has higher costs compared to the conventional direct scheme in the case of the mixtures with unbalanced ease of separation (SI=0.47, 1.74). The FTCDC proves to be inefficient for these separation tasks.

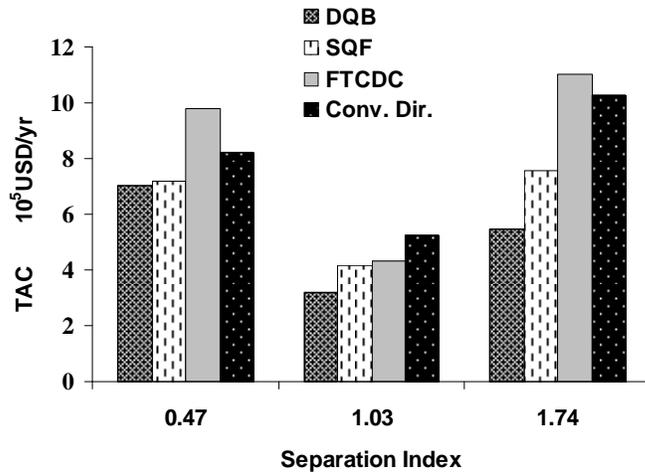


Figure 13 TAC vs. SI when the required product purity is 95%.

The results of the economic study in the case of 99% product purity (**Figure 14**) show that the most economic distillation structure is the DQB and only in the case of mixture with SI=0.47 it is SQF. Although the SQF is not the most economic structure in every case, but it is not as sensible to the increase of product purity as other structures.

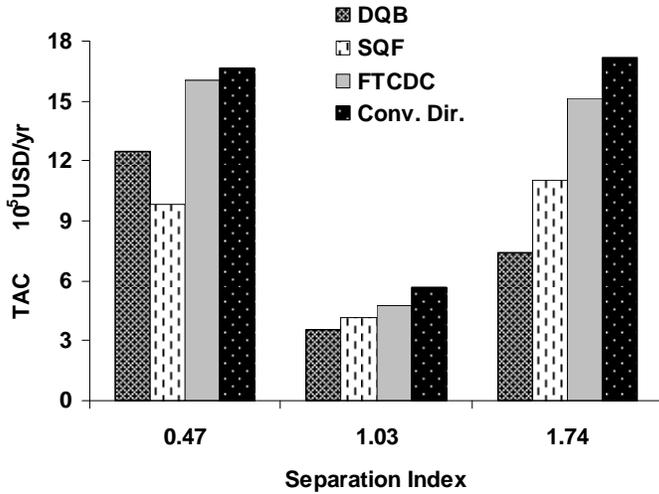


Figure 14 TAC vs. SI when the required product purity is 99%.

It follows from **Figure 12–11** that the TAC has an increasing tendency with the increase of the product purity which correlates with the raised energy usage of high product purity distillations. The studied distillation schemes run with the lowest costs when the ease of separation is balanced (SI=1.03) and the heat-integrated systems (DQB, SQF) are the most economic arrangements in almost every case and it is always better than FTCDC. The results of the economic study correlate with the results of the exergy analysis.

Results of GHG emission estimation

The GHG emissions of the studied energy-integrated distillation systems are estimated and compared to the emission of conventional distillation scheme. The major emission related to the distillation systems of the case study is the GHG emission caused by the large heat requirement of these systems. Therefore, the energy requirements of the different distillation systems are calculated. Based on the energy consumption data of the distillation schemes, GHG emissions are estimated using SimaPro 6.0 and the results are verified by the model developed by Gadalla et al.²⁴ for quantifying the emissions associated with distillation systems. Reducing energy requirements of distillation systems leads to lower GHG emission; this is why reconsideration of the design methodology is necessary. Energy integration could be a solution to reach a lower GHG emission through

better energy utilization. Carbon dioxide equivalent is used in order to quantify these emitted GHG (eq 19). The global warming potential (GWP) values of the GHG are taken for 100 years time horizon (Table 2). This CO₂e emissions are estimated assuming four different fossil fuels as heat source: natural gas, oil, coal, and lignite. The emitted greenhouse gases using these fossil fuels are composed mainly by CO₂ and by slight amount of N₂O and CH₄. The amount of emitted halogenous compounds is practically negligible compared to the CO₂ emission and therefore it can be neglected.

Appropriate firing equipment is selected for each kind of heat source based on the descriptions found in the literature ⁵¹:

- Natural gas heated atmospheric burner with low NO_x emission with efficiency $\eta=87\%$.
- Fuel oil (low sulphur) boiler under 100 kW with efficiency $\eta=87\%$.
- Industrial coal furnace used in range of 1-10MW with efficiency $\eta=80\%$.
- Stove lignite briquette 5-15kW with efficiency $\eta=70\%$

The results show that the investigated energy-integrated distillation systems have lower CO₂e emission compared to the conventional direct distillation scheme. The energy requirement and consequently the associated CO₂e emission grow with the increase of the product purity. This tendency is valid for all of the studied distillation systems but the SQF is the least sensitive (**Figure 15**).

Energy-integration of the distillation columns can reduce the CO₂e emission and further minimization of this emission can be reached by using cleaner fossil energy source.

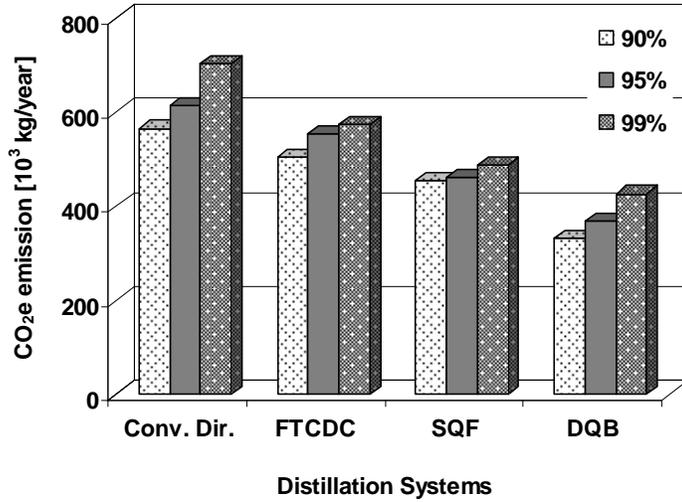


Figure 15 CO₂e emission of the studied distillation systems at different product purities in case of mixture with SI=1.03, with natural gas as fossil fuel.

Figure 16 shows the CO₂e emissions of the four studied distillation systems in case of the different fossil fuel used as heat source. CO₂e emission is the lowest when natural gas is used as heat source in the case of each studied distillation scheme. This tendency is true for each studied separation problem.

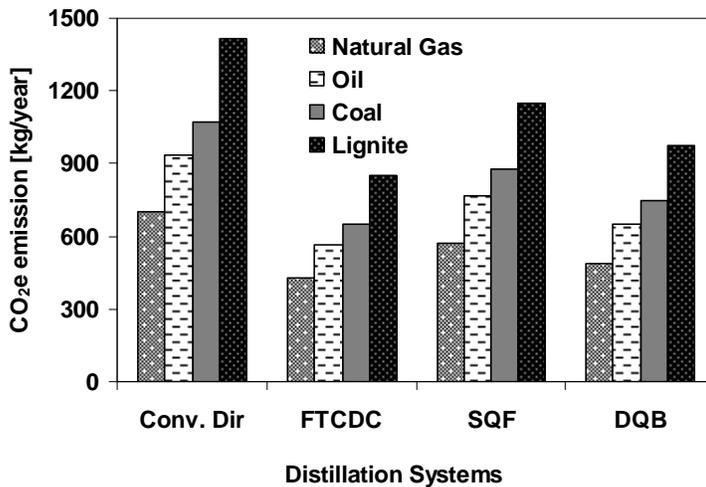


Figure 16 CO₂e emission of fossil fired distillation structures, the product purity is 95%, mixture with SI=1.03.

The CO₂e emission increases if the ease of separation is not symmetric that is when separation index (SI) is far from 1 (**Figure 17**).

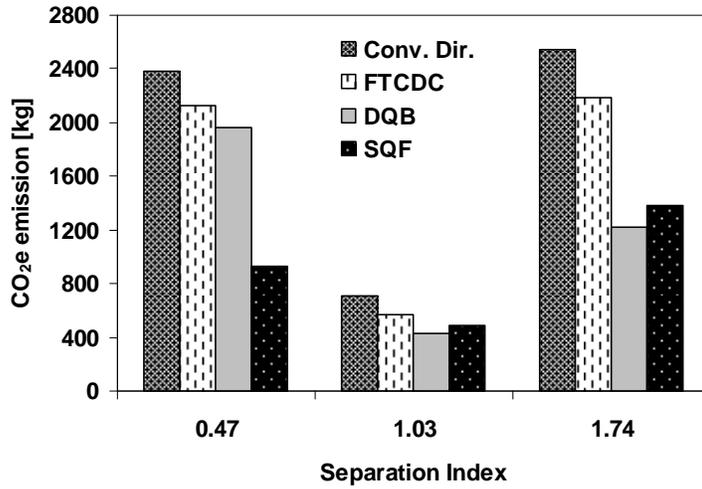


Figure 17 CO₂e emission of the distillation systems, in the case of different ternary mixtures. The required product purity is 95% and with natural gas as fossil fuel.

The CO₂e emission reduction compared to the base case is also investigated. The CO₂e emissions are summarized for all three product purities into one average CO₂e emission saving figure. These figures are shown in one chart (**Figure 18**) for all the three studied energy-integrated distillation schemes.

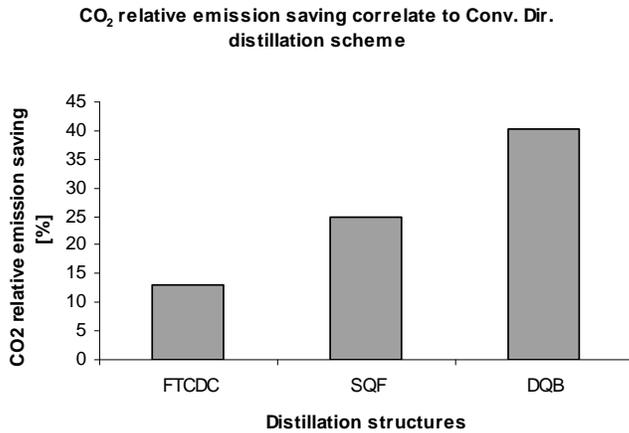


Figure 18 CO₂e relative emission saving compared to the conventional direct distillation scheme.

Figure 18 shows that the DQB structure has the best performance that means, the DQB scheme is the most flexible in the CO₂e emission issue if product purity alters. The average emission saving of DQB reaches 40%. The CO₂e emission confirms the results of the previous studies of this work and draws the attention to the consequences of wasted energy.

Ranking the process alternatives

The ranking of process alternatives is based on the different process indicators from the exergy analysis, economic study, and the GHG emission estimation. The indicators are numerically presented in the Figure 9, Figure 13, Figure 17 and they are transformed into an individual desirability value d from 0 to 1. In the case of thermodynamic efficiency, maximization is desirable, while the TAC and CO₂e emission should be minimized. The weighting factors of the different indicators are taken equally 1 in this case study; however, the desirability function method allows the use of weighted indicators if the criteria are not equally important. According to the equation 20, D_{fct} is calculated and presented in function of the different ternary mixtures and the investigated distillation systems (**Figure 19**).

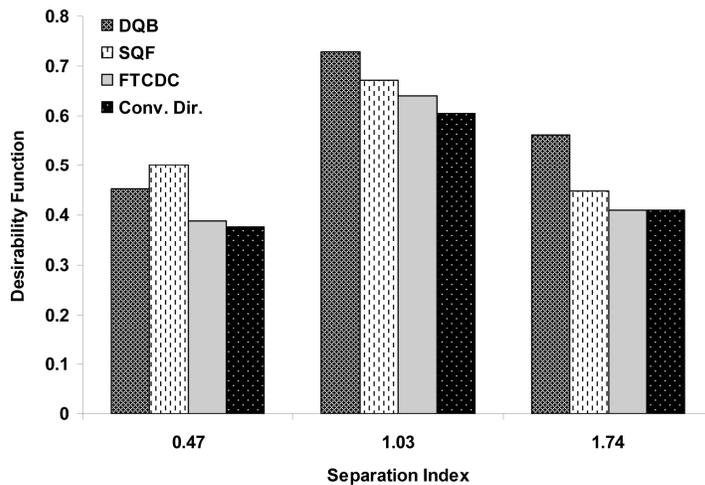


Figure 19 D_{fct} vs. SI for the studied distillation systems.

Decision

The complex evaluation methodology reveals that the most adequate distillation system is the SQF in the case of the mixture with SI=0.47 and the DQB in the case of the mixtures

SI= 1.03 and 1.74. The case study investigations prove that the results of the exergy analysis are in linear correlation with the economic features as well as with the emissions. The methodology for the estimation of the different process design alternatives can become quite simple. We can conclude that the results of the exergy analysis are in strict correlations with the results of the economic, and environmental analysis. Therefore, it can be concluded that the determination of thermodynamic efficiency on exergy analysis basis is satisfactory for the evaluation of the different design alternatives. Considering that the proposed methodology can be used in the process design stage of distillation systems, the basic assumption of the process design should be applied also in this methodology. The basic assumption is that the ambient parameters should be identical in each case. It means that the temperature, pressure, and compositions of the input and output streams must be the same for each process design alternative.

4.7 Conclusions of the complex evaluation methodology application

The proposed process investigation methodology for distillation systems helps to evaluate process alternatives from a complex point of view. Following this methodology, the problem defined on the first level is suitable for the complex comparative study. The second level is the multicriteria evaluation and it forms the hearth of the methodology. On this level three different kinds of analysis are carried out in order to evaluate the distillation systems based on exergetic, economic, and environmental impact aspects. On the last level of the methodology these three aspects are aggregated by the D_{fct} in order to help the selection of the most adequate distillation design alternative giving one general characteristic figure for each process design alternative.

In the case study, three energy-integrated distillation systems are investigated and compared to the conventional direct scheme. The input / output parameters and the system boundaries are defined similarly for these investigated systems. In the case of the exergy analysis the base of comparison is their thermodynamic efficiency. This analysis shows that the heat-integrated distillation structures (DQB and SQF) are the most energy-efficient among the studied ones. The thermodynamic efficiency of all the studied distillation systems is the highest when the ease of separation is symmetric, that is, the

exergy loss is minimal in analogue cases. Economic study supports the results of the exergy analysis and shows that the heat-integrated distillation structures have the best economic features as well. Although the FTCDC is less economic than the other investigated heat-integrated systems but it shows energy savings compared to the conventional sequence. CO₂e emission reduction can be achieved with the use of cleaner fossil energy source, and using heat-integrated distillation schemes. CO₂e emissions of the distillation systems can be decreased by an average 40% using DQB arrangement instead of conventional alternative. The CO₂e emission estimation demonstrates that in most cases, the DQB has the lowest CO₂e emission but the SQF is less sensitive to product purity change.

Applying the D_{fet} reveals that among the different distillation schemes, the heat-integrated DQB alternative proves to be the best applicable, since it shows the features in a wide and flexible range.

This work also shows that the thermodynamic efficiency determined during exergy analysis predicts the results of the economic study and provides further information about the system. Based on these results one can conclude that the generally favoured economic study can be replaced with exergy analysis in the early stage of process design. Moreover, the exergy analysis can also predict the emissions associated with the utilized energy and this proportionality can simplify the decision making during the process synthesis step. This emphasizes the improving importance of the exergy analysis also in the process design practice.

Chapter 5 Retrofit design of an industrial heat-integrated distillation system

5.1 Introduction

This chapter presents a retrofit design of an existing industrial heat-integrated distillation system consisting of three columns originally. The retrofit design case study gave the possibility to study the heat-integration in industrial scale and to investigate the energy-integration in the case of polar mixture; therefore, this case study serves as a completion of the previous studies for hydrocarbon mixtures.

The task was to examine how the capacity of the separation system could be increased by 42.8% and to increase the energy saving performance. Based on the previous evaluation study the backward heat-integrated solution is investigated for the given N, N-dimethylformamid - water mixture. The performance of the existing distillation system and of various increased-capacity structures have been studied using rigorous process simulation.

N,N-dimethylformamid (DMF) is a well known solvent of many hydrophobic organic compounds. DMF is also used as crystallization medium in the pharmaceutical industries but the main consumer of DMF is the polymer industry. Production and processing of polyamide and acrylic fibers, films, coatings and wire enamels all require the usage of DMF. The solvent spinning process that is used for the production of polyamide fibers uses large amounts of DMF. The polymer is dissolved in DMF resulting in a solution that is suitable for extrusion through a spinneret. The extrusion is followed by the precipitation of the polymer fiber with the help of an aqueous bath. In the last step of the technology the DMF is recovered from an aqueous solution, so it can be reused as a solvent.

DMF-water mixtures are separated using distillation. Although the DMF and water constitute an ideal mixture and could be separated in a single distillation column, in the industrial practice usually a two-column heat-integrated sequence is used for the

separation. The initial ca. 40 wt% DMF containing solution is fed into a vacuum column. The top product of the vacuum column is pure water; the bottom product enriched in DMF is fed into the second column that is operated at atmospheric pressure. The bottom product of the atmospheric column is 99.99 wt% DMF, while the top product of the atmospheric column is 99.9 wt% water. The overhead vapour of the atmospheric column provides the heat that is necessary for boiling up the vacuum column. The condenser of the atmospheric column and the reboiler of the vacuum column are replaced by a single heat exchanger. This arrangement is called direct distillation sequence with backward heat integration.

5.2 The aim of the retrofit design work

The general aim of this work is to suggest process modifications that enable the capacity increase of an existing DMF-water separation system that is operated at the site of a Hungarian polymer fiber production plant. The performance of the existing energy-integrated distillation system and of various increased-capacity alternatives are studied using rigorous process simulation. Process modifications are suggested based on the simulations exclusively.

5.3 Description of the existing separation process

Scheme of the DMF recovery system of an existing Hungarian polymer fiber production plant is shown in **Figure 20**. The DMF is recovered from 14 tons/h 60 wt% water containing aqueous solution.

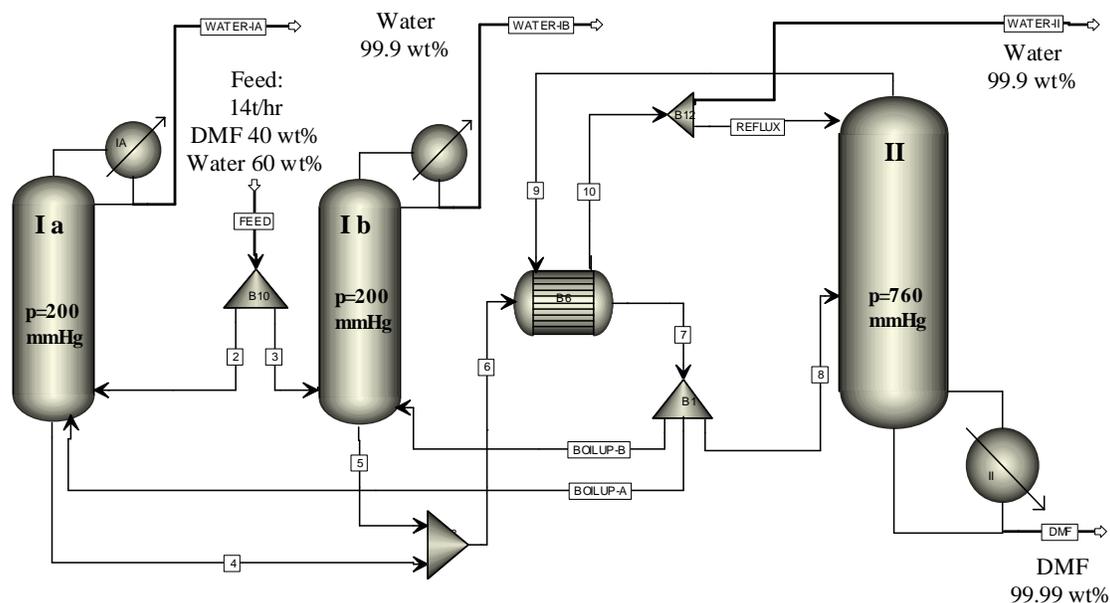


Figure 20 The original DMF-water separation system with backward heat integration.

At this particular plant the crude DMF solution is fed into two parallel connected distillation columns: Ia, Ib that are operated at 200 mmHg vacuum. The column internal of these two columns is an older type of Sulzer Mellapak structured packing. The vacuum columns produce 99.9 wt% water containing distillate and a bottom product that contains approximately 60 wt% DMF and 40 wt% water. The vapour phase bottom products of the vacuum columns are fed into an atmospheric pressure distillation column (column II), that contains trays as column internals. Column II produces a 99.9 wt% water containing distillate and extremely pure (99.99 wt%) DMF in the bottom. The latter is the main product of the separation system. Low water content of the purified DMF is a key factor of the polymer fibre production.

All relevant data of the existing separation system and distillation columns are known, except for the exact type of structured packing that is installed in the vacuum columns. The columns are heat-integrated; the overhead vapour of the atmospheric column boils up the parallel connected two vacuum columns (**Figure 20**). The capacity of the existing separation structure is 14 t/h that has to be increased up to 20 t/h.

5.4 Simulation of the existing separation process

Simulation of the existing separation system was carried out at first. This study deals with the basic chemical engineering retrofit design of the system, therefore, pumps and other supplementary technological elements are not considered in the simulations. For the sake of simplicity, the two parallel connected vacuum columns are simulated as a single distillation column. Structure of the original separation system - as it is simulated - is shown in **Figure 21**

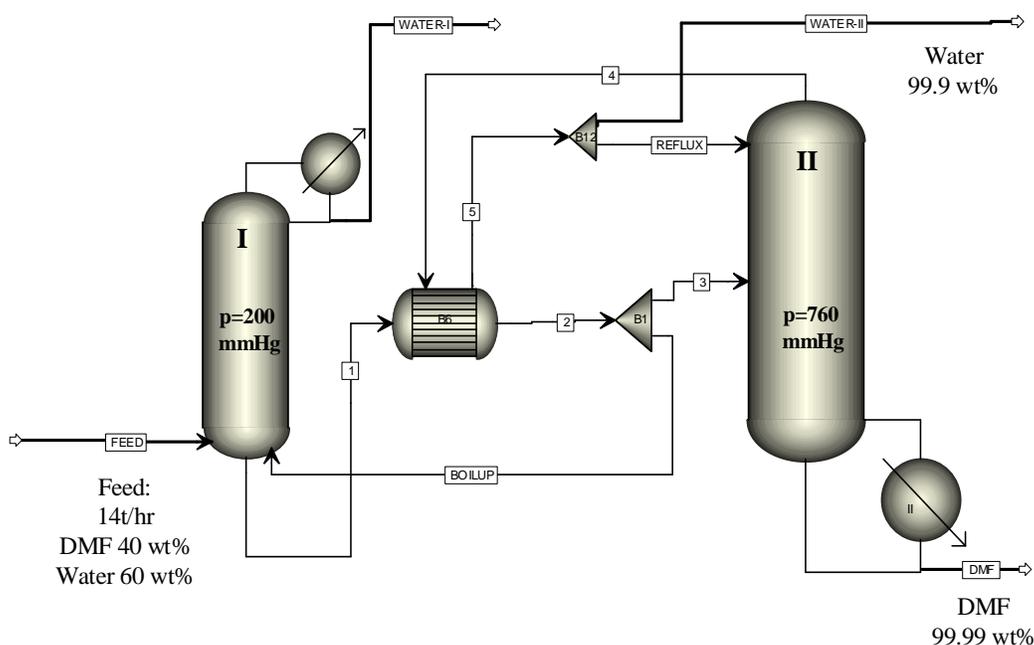


Figure 21 Simulation of the original DMF-water separation system.

Simulation calculations were carried out using the ChemCad 5.1.3 and the Aspen Plus 12.1 process simulators. In order to avoid numerical difficulties, simulation of the system shown in Figure 21 is built up in a stepwise manner:

- First, the two parallel vacuum columns have been simulated (as one column)
- Second, atmospheric distillation column had been added
- Finally, the heat-integrated separation system was simulated

The UNIQUAC model is used to calculate vapour-liquid equilibrium. Specifications of the columns of the existing separation system are shown in **Table 6**.

Table 6 Specifications of the columns of the existing separation system

	Column I (200 mmHg)	Column II (760 mmHg)
Pressure (mmHg)	200	760
No. of theoretical trays	16	27
Feed stage	16	17
Feed thermal condition	Partially vaporized	Totally vaporized
Reflux ratio	0.57	0.86
Column diameter (mm)	Column Ia: 1000 Column Ib: 1400	2000

As **Table 6** shows, the packed vacuum columns is simulated as if they were columns with trays. Numbers of theoretical trays of the packed columns is calculated using the packed height of the columns and HETP vs. F factor diagram.

The height equivalent to a theoretical plate (HETP) is a key parameter for describing mass-transfer efficiency in structured packing. This HEPT is the height of packing that is required to produce an ideal separation where the exiting vapour and liquid are in thermodynamic equilibrium. Column designers use the HETP to calculate the height of packing necessary to achieve a given separation. The HETP depends on the geometry of the packing, the physical properties of the chemical system, and the operating conditions of the column.

The HETP-F factor diagram of the assumed type of Sulzer packing (presumably Sulzer Mellapak 250-350, regarding that the present separation system was built in the early eighties) is used for calculations. Since aqueous mixtures do not wet the packing with efficiency as it is assumed in the Sulzer HETP-F factor diagrams, the value of the theoretical trays obtained this way had to be divided by two. According to Kister⁵², separation efficiency of the Sulzer Mellapak packings in case of rectifying aqueous mixtures is half of the efficiency that can be observed in case of organic mixtures.

Simulation calculation of the existing separation process gave back exactly the flow rate and composition data of the columns that could be measured in the plant. From the point

of view of heat integration, the most important data are the heat duty and temperature of the condenser of the atmospheric column, and those of the reboiler of the vacuum column. These data are shown in **Table 7** and **Table 8**. As these tables show, both the temperatures and the heat duties enable heat integration between the two columns. Heat duty values of **Table 7** show that the condenser of the atmospheric column provides more heat than it is necessary to boil up the vacuum columns. In reality the difference between the absolute values of the heat duties is the heat loss of the existing system (around 12%). When simulating the heat-integrated model a trim condenser was used to account for the heat loss.

Table 7 Reboiler data of the vacuum columns

	Bottom temperature [°C]	Reboiler heat duty [kW]
Column I (200 mmHg)	70.47	4265.03

Table 8 Condenser data of the atmospheric column

	Top temperature [°C]	Condenser heat duty [kW]
Column II (760 mmHg)	99.63	-4887.14

Usually, the least expensive way of increasing the capacity of existing distillation columns is the replacement of the original column internals with new, high efficiency structured packings. Selection of the packing type requires column vapour load data. Simulated liquid and vapour flow rates of the vacuum and of the atmospheric columns are shown in **Figure 22** and **Figure 23**.

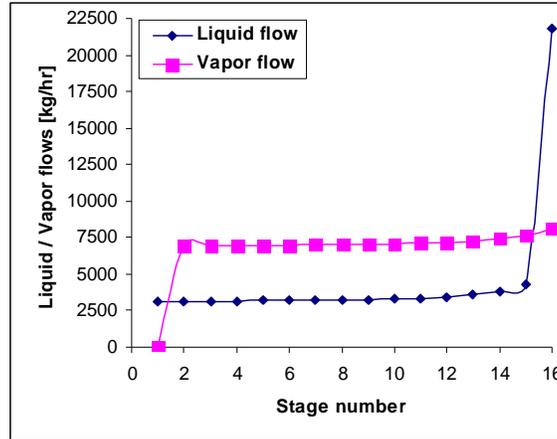


Figure 22 Internal vapour and liquid flows in the vacuum column (column I).

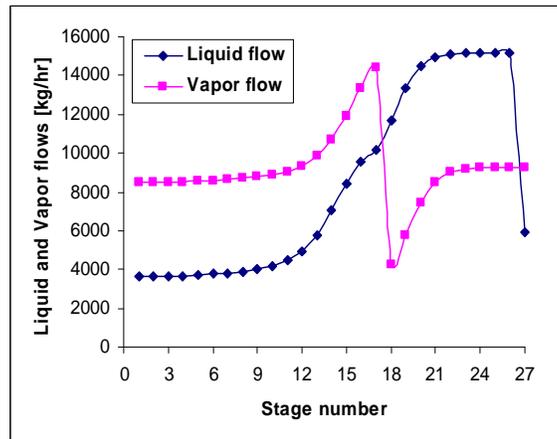


Figure 23 Internal vapour and liquid flows in the atmospheric column (column II).

The most important data for column sizing is the vapour flow rate. As the figures above show, the highest vapour flow rates in both columns occur at the feed stages. These maximum vapour flow rates are to be taken into account when calculating the optimal column diameters or when calculating the performance of a column at a given diameter.

5.5 Retrofit scenarios and calculations

There are many conceivable ways in which the capacity of the entire system could be increased from 14 tons/h to 20 tons/h. We have considered the following scenarios:

- A. It is not necessary to change the structure of the system. Simply by increasing the feed flow rates of the columns will do; the system will keep its separation efficiency.
- B. Replacing the internals/packings of some of the existing columns or installing new high efficiency packings in all of the columns.
- C. Addition of the available extra column and installing new high efficiency packings in some/all of the columns.

Scenario A is not a real opportunity. If the problem could have been solved this way than the operators of the plant already could have increased the capacity. Installation of new, high efficiency packings is necessary by all means.

Capacity calculation of the columns is carried out according to the F factor method⁵³ using the available HETP-F factor diagrams of the different types of new Sulzer Mellapak packings⁵⁴. The F factor method requires the calculation of the maximum vapour flow rate, the maximum vapour density, and the knowledge of the column cross sections. The F factor can be calculated according to equation 21.

$$F_{factor} = V_m * \sqrt{\rho_v} \quad (21)$$

where V_m is the maximum superficial vapour velocity [m/s] and ρ_v is the maximum vapour density [kg/m³] in the column. Vapour velocity can be calculated using equation 22:

$$V_m = \frac{\dot{M}_{max}}{\rho_v * A * 3600} \quad (22)$$

where \dot{M}_{max} is the maximum vapour flow rate [kg/h] and A is the cross-sectional area of the distillation column [m²].

In this case, the cross sectional areas of the columns are given. Maximum vapour flow rates and vapour densities are calculated using the process simulation program (**Figure 22** and **Figure 23**). In the following, detailed calculations of the individual distillation columns are shown.

5.5.1 Existing vacuum columns

These are columns Ia and Ib that are operated at 200 mmHg pressure. Parameters required for the F factor calculation in case of 14 tons/h feed flow rate are the following:

Maximum vapour flow rate: $\dot{M}_{max} = 8150.6 \text{ kg/h}$ (as shown in Figure 22)

Maximum vapour density: $\rho_v = 0.1982 \text{ kg/m}^3$

Using the parameters of columns Ia, Ib the value of the F factor can be calculated for the increased capacity (20 tons/h). The summed cross sectional area of the two columns is 2.32 m^2 . The maximum vapour flow rate shown in **Figure 22** is to be multiplied by 1.42857 (20/14 tons/h). Using equation 21 and 22 the value of the F factor results in 3.13, this is multiplied by a safety factor of 1.2. Applying a safety factor is usual; in this case it allows 20% positive deviation from the planned feed flow rate. Accordingly, the final value of the F factor is 3.756. **Figure 24** shows the HETP-F factor function measured for the Sulzer Mellapak 250.Y, and Mellapak Plus 252.Y packings. These packings are the latest products of Sulzer Chemtech.

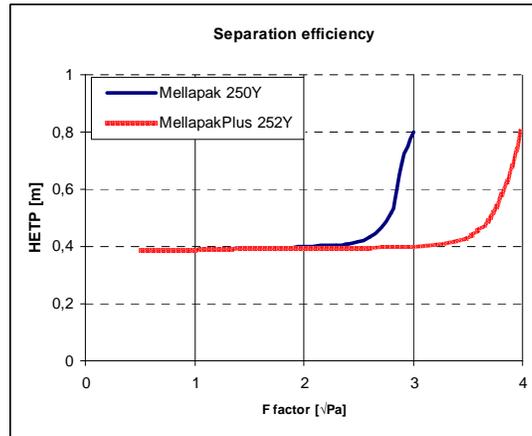


Figure 24 Separation efficiency of Sulzer packings at 200 mmHg.

As **Figure 24** shows, the separation efficiency of Sulzer Mellapak 250.Y packings is falling at F factor values greater than 2.5 and the separation efficiency of Sulzer Mellapak Plus 252Y starts to fail at 3.5 F factor value. This way it is proven that the vacuum columns with increased capacity (20 tons/h; $F=3.756$) could not satisfy the given purity requirements; capacity increase of the vacuum columns cannot be achieved by installing

new high efficiency packings. Retrofit scenarios A and B do not work, addition of the available extra column is necessary.

5.5.2 Extra column connected parallel to the vacuum columns

The available extra column (Ic) can be used for increasing the capacity of the vacuum part of the separation system if it is connected parallel to columns Ia and Ib. In this case all three columns are operated at 200 mmHg. The diameter of the available column is 1100 mm. The total cross-sectional area that can be reached this way is 3.275 m² (columns Ia, Ib, Ic together). Using this cross-sectional area and the maximum vapour flow rate, the value of the F factor results in 2.22 for 20 tons/h feed. Using a safety factor of 1.2 again, the final value of the F factor becomes 2.664. **Figure 24** shows that at this F factor value the separation efficiency of the Sulzer Mellapak 250.Y and 252Y packings just begins to deteriorate. Simply just replacing the packings and connecting the available column parallel to the existing vacuum system is not a safe solution, because at increased capacity (20 tons/h) the system would work at its upper capacity limit.

Still, capacity increase can be safely achieved when adding 3 more meters to the packed height of the available extra column (Ic), and when using the Mellapak Plus 252Y structured packing in all three columns (Ia, Ib, Ic). Adding 3 meters to the hull of column Ic can be carried out by the technicians on-site, relatively easily at moderate cost.

5.5.3 Atmospheric column

The atmospheric column is marked column II in **Figure 21**. The course of the capacity calculation is similar to the previous calculations.

In case of 14 tons/h capacity, the maximum vapour flow rate in column II is 14442 kg/h and the maximum vapour density (ρ_v) is 2.096 kg/ m³. The diameter of column II is 1m. Using a safety factor of 1.2, the F factor value in column II for 20 tons/h capacity is 1.512. As **Figure 25** shows, Column II could easily handle the increased capacity when it would be re-filled with Mellapak 250Y or 252Y packings.

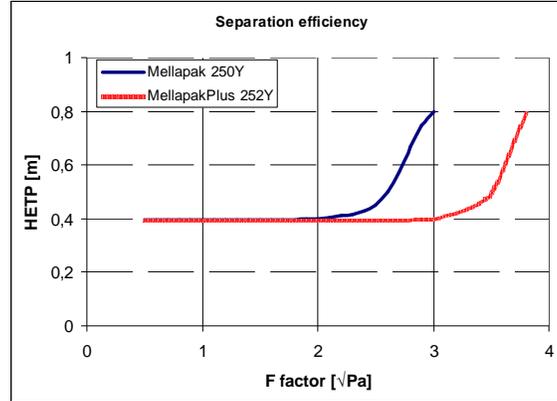


Figure 25 Separation efficiency of packings at 720 mmHg.

Since the existing packings of the vacuum columns (Ia, Ib, Ic) are to be replaced by Mellapak 252Y packings anyway, it is recommended to use the same type of packings in the atmospheric column (column II), too. This way the atmospheric column will work far under its capacity limit, and can equalize the incidental vapour flow upsurges that may occur due to the actions of the process control system.

5.6 Suggested retrofit design

Concluding the results of the calculations that is carried out up to this point, it can be stated that the capacity increase from 14 tons/h to 20 tons/h is possible, provided with the following process modifications:

- The packed height of the available extra column (Ic) is to be elongated by 3m and the column is to be connected parallel to the existing two columns (Ia, Ib) of the vacuum part of the system.
- The internals of all the four columns (Ia, Ib, Ic, II) are to be replaced by 252Y type of Sulzer Mellapak Plus structured packings.

The suggested retrofit design that can handle the increased 20 tons/h DMF-water feed is shown in Figure 26. Discussions with the plant managers made it clear that the suggested

retrofit design is the most economical solution that can be found for the capacity increase problem.

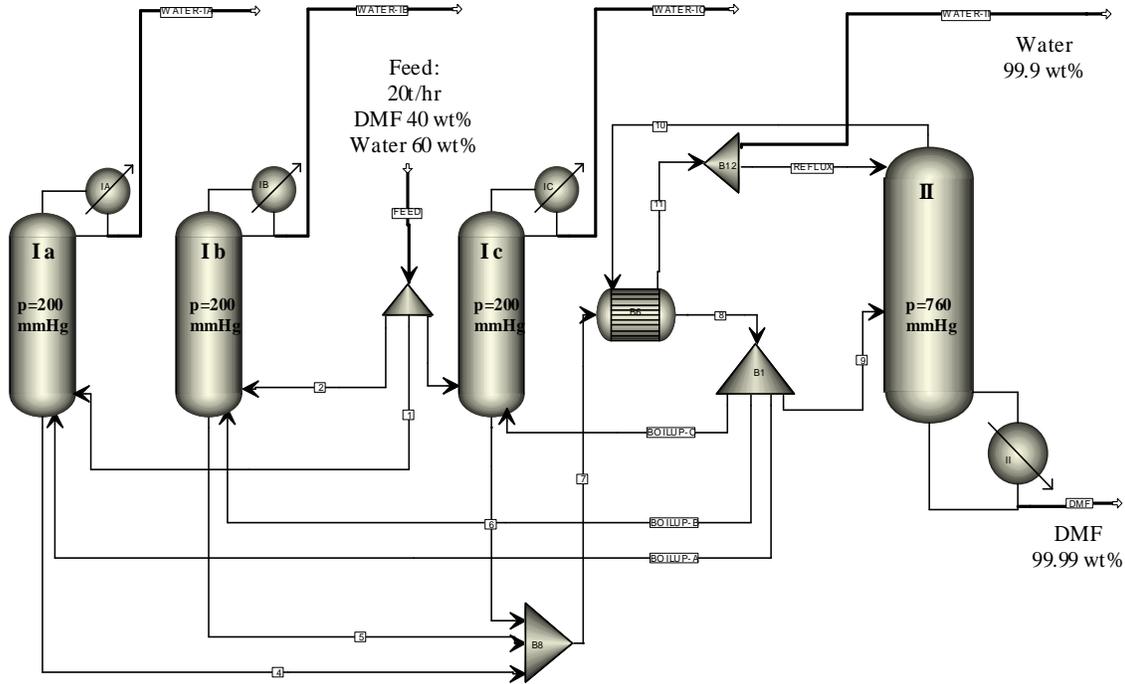


Figure 26 Heat-integrated retrofit design for the separation of 20 tons/h DMF-water mixture.

In order to estimate the operating cost of the retrofit structure, energy requirements of the individual distillation columns and the energy requirement of the whole separation system have been calculated. Major results are shown in line 3 of **Table 9**. Lines 2 shows the energy requirement of the present heat integrate lower capacity system. For the sake of comparison, line 1 shows the energy requirement of the lower capacity system, supposing that there is no heat integration. As **Table 9** shows, energy integration results in large energy savings. The increased-capacity energy-integrated separation system consumes about half of the energy that would be required for the operation of the non energy-integrated system at lower capacity.

Table 9 Energy requirement for the recovery of DMF

Distillation sequence	Feed flow rate [tons/h]	Heat duty of the condensers [kW]	Heat duty of the reboilers [kW]	Total heat duty [kW]
2+1 columns without heat integration	14	9129.2	9635.8	18765
2+1 columns with heat integration	14	5313	1392.6	6704.6
3+1 columns with heat integration	20	7445	1924.6	9369.6

The results are even more interesting when the heat duties are related to the mass flow rate of the recovered pure DMF solution. Table 10 shows the calculated energy requirements for the recovery of 1 kg DMF. The reduction of the energy consumption by using energy-integrated system is 64.26% in case of original capacity (feed: 14 tons/h) and 65.04% in case of increased capacity (feed: 20 tons/h).

Table 10 Energy requirement for the recovery of 1 kg DMF

Distillation sequence	Feed [tons/h]	Condensers heat duty [kW]	Reboilers heat duty [kW]	Total heat duty [kW]
2+1 columns without heat integration	14	0.65208	0.68827	1.34035
2+1 columns with heat integration	14	0.3795	0.0995	0.4789
3+1 columns with heat integration	20	0.3722	0.0962	0.4685

Comparing the values of the last column of Table 10 clearly shows that the heat-integrated distillation system obtained by the retrofit design has the lowest specific energy consumption.

5.7 Conclusions

It can be concluded that increasing the capacity of the heat-integrated separation system from 14 tons/h to 20 tons/h is possible. The extra column that is available on-site is to be elongated by 3m, and is to be connected parallel to the existing two columns of the vacuum part of the separation system. The internals of all the columns are to be replaced by new, high efficiency Sulzer Mellapak Plus 252Y structured packings. Energy requirements of the recovery of 1kg DMF have been calculated for both the existing and for the suggested retrofit structure. The results show that the heat-integrated distillation system obtained by the retrofit design has somewhat lower specific energy consumption compared to the existing heat-integrated separation system, while its capacity is increased by 42.8%. The study shows that the energy integration principles can be applied on polar binary mixture separation as well.

The industrial case study is an example of the successful application of the process design principles obtained at the investigation of the energy-integrated distillation alternatives in this work.

Chapter 6 Operability evaluation of the energy-integrated distillation systems

The operability of the energy-integrated distillation systems is an important criterion during the design phase and it has to be taken into account before applying a specific energy-integration beside of the energy-saving, economic or environmental properties. Since the operating cost is the main part of the total annual cost it is important to operate the distillation systems in their optimal range. Thus, the controllability study has to become the integral part of process design tasks and should be completed in the early stage of the process design. The operability of the process unit can be analyzed with different tools such as controllability study of the steady state model or in frequency domain. More reliable investigation can be carried out with load rejection analysis in time domain that requires the dynamic model of the process unit. This latter analysis is a time and energy consuming investigation.

The controllability study predicts the dynamic behaviour of the distillation system. The task is to foretell how controllable the process is, can it handle large disturbances or how robust it is. The operability of distillation systems depends on their controllability and dynamic behaviour.

The aim of this chapter is to elaborate an easy applicable controllability analysis method in order to compare energy-integrated distillation systems based on their control properties and to select the easiest controllable one. This chapter verifies the results of the proposed controllability study with load rejection analysis. The controllability analysis method is described as follows.

6.1 Controllability analysis of the distillation systems

6.1.1 The selection of the controlled and manipulated variables

The first step of the analysis is the selection of the controlled and manipulated variables for the investigated systems. Considering a simple two product distillation column, the column has two degrees of freedom, which may be used to specify top and bottom compositions. The distillation column is a 5×5 system: the controllers manipulate all five inputs (L, B, V, D, Q,) in order to keep the five outputs (reflux drum level and column bottom level, pressure, top and bottom product composition). Since the levels and pressure must be controlled at all times to ensure stable operation, the level and pressure loops are designed first³² and in the next step the composition control loops can be designed for the distillation column.

6.1.2 Calculation of the controllability indices in frequency domain

The controllability analysis is carried out by calculating the transfer function matrices (G) for open-loop control systems. These transfer function matrices are subjected to Singular Value Decomposition (SVD) described in Chapter 1. Based on SVD the controllability indices can be calculated. These controllability indices are used to predict the degree of directionality and the level of interactions in the system. The analysis is performed in the frequency domain calculating frequency dependent indices which may yield additional information about the investigated system⁵⁵. It is important to note that the values of the controllability indices should be read in the range of the critical frequency that is calculated for each system in open-loop and in function of the time constant which results from the response of a step disturbance.

$$\omega_{crit} = \frac{2\pi}{T_{ol}} \quad (23)$$

where the ω_{crit} [rad/sec] is the critical frequency and T_{ol} [sec] is the time constant.

6.1.3 Aggregation of the controllability indices

The specialized literature traditionally considers the different controllability indices individually; however, they may show opposite controllability characteristics for a given control structure. The results of the controllability study are often difficult to interpret because of the controversial index results for the investigated system (e.g. the value of the CN is close to the desirable band but the RGA value indicates strong interactions).

In order to aggregate the different controllability indices my thesis proposes a method to optimize the multiple control characteristics problems. This method usually is applied in statistics and it is called the desirability function (D_{fct}) previously described in Chapter 3.

In this chapter the method of desirability function is used to select control structure for energy-integrated distillation systems with the best controllability characteristics such as CN, MRI and RGA in frequency domain.

The individual desirability functions, d are continuous functions and they are chosen from among a family of linear or exponential functions. The overall desirability function D_{fct} is defined as the geometric average of the individual desirability functions.

The used individual desirability functions have the following specification:

- a) The CN value below 10 indicates a well-conditioned system and in this range the d_{CN} approaches 1 which is desirable. A transfer matrix with CN larger than 10^3 is considered ill-conditioned. The value of d_{CN} is close to 0 at large CN values ($>10^3$) but it is not zero, thus the control structure is not excluded only because of its large CN. The chosen d_{CN} function, which describes the previously mentioned criteria has the following form (equation 24)

$$d_{CN} = \exp(-(a + b \cdot CN)) \quad (24)$$

- b) The large MRI value predicts resilience process which can deal effectively with disturbances. The maximization of this individual response is desirable. Thus, the function of d_{MRI} has the form presented in equation 25. The d_{MRI} function gives low d values for MRI values lower than 10^{-2} and highly discriminates the MRI parameters between 10^{-2} and 1 since the most of the investigated control structure have its MRI in this range.

$$d_{MRI} = 1 - \exp(-MRI \times 10) \quad (25)$$

- c) Small values of RGAno indicate a preferable variable pairings with less interaction. Therefore the minimization of this individual response is advantageous. The chosen function d_{RGAno} favours RGAno values lower than 1 and its value abruptly decrease at higher values than 1.

$$d_{RGAno} = \exp\left(-\frac{RGAno}{10}\right) \quad (26)$$

6.1.4 Ranking of the studied distillation systems

Based on the D_{fct} the studied distillation systems are ranked. High value of D_{fct} shows that all d are toward the target value which indicates that the system has good controllability features.

The thesis contains a verification study of the proposed control properties evaluation analysis. The controllability analysis is applied on the studied distillation systems and the results are verified with closed loop simulations in time domain.

6.2 Application of the controllability analysis on the investigated distillation systems

Composition control is realized at the studied distillation systems; therefore mole fraction is selected as controlled variable.

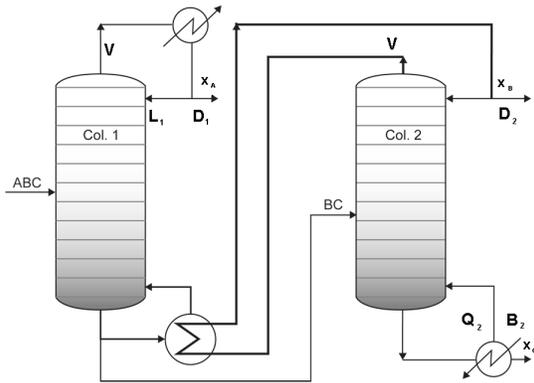
The selection of the manipulated variable pairings among the possible ones is based on closed-loop simulations since the publications in the literature do not consider reliable the selection based on controllability indices³³. The selected manipulated variable pairing for the investigated distillation systems are presented in the **Table 11**. Ratio control is not considered in this work.

Table 11 Selected manipulated variable pairings

Distillation systems	Manipulated variable pairings
DQB	$D_1L_2B_2$
FTCDC	LSQ
SQF	LSB
Conv. Dir.	$D_1L_2B_2$

The chosen manipulated variables are: L – reflux rate of the respective column (kmol/h); D – distillate flow rate of the column (kmol/h); B – bottom product rate of the column (kmol/h); Q - heat duty of the column's reboiler (kW). The operating conditions selected for controllability study are: pentane- hexane- heptane ternary mixture with equimolar feed composition and 95% product purity.

In the case of the studied energy-integrated distillation systems the controlled and manipulated variables are shown on Figure 27-28.

**Figure 27** DQB indicating its controlled and manipulated variables.

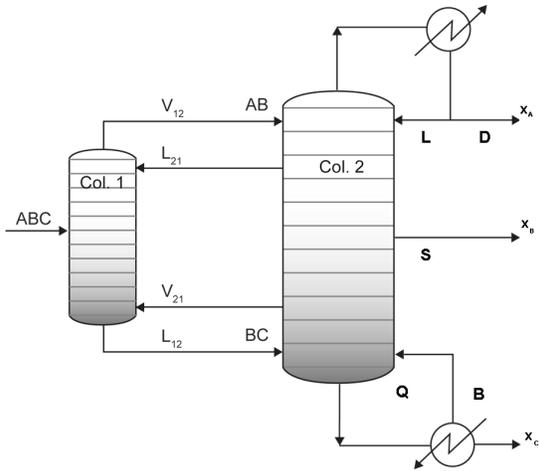


Figure 28 FTCDC indicating its controlled and manipulated variables.

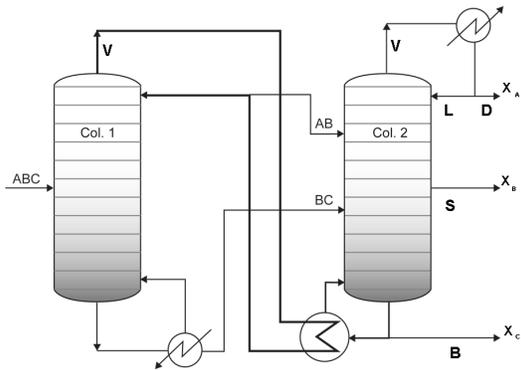


Figure 29 SQF indicating its controlled and manipulated variables.

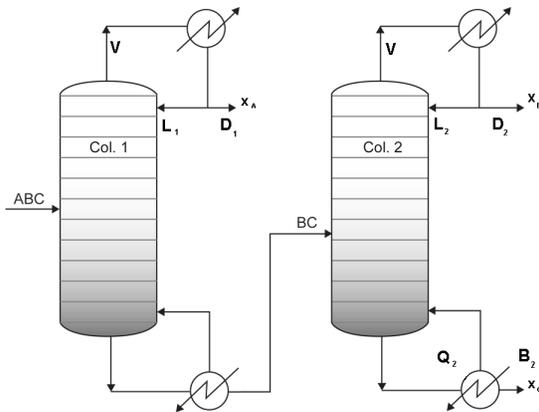


Figure 30 Conv. Dir. indicating its controlled and manipulated variables.

The frequency dependent controllability indices (CN, MRI, RGAno) are calculated and presented in Figures 31-33. The values of the controllability indices that count in the range of the critical frequency are calculated for each system in open-loop in function of the time constant which results from the response of a step disturbance. The values of the critical frequency of each distillation system differ and they range between 10^{-3} and 10^{-2} [rad/sec].

The **Figure 31** shows the condition number in function of frequency. Based on the CN values, the ranking of the studied distillation systems in sense of controllability would be: the easiest controllable systems are the DQB and SQF followed by the FTCDC, and Conv. Dir. shows the worst control properties (Table 12). If the MRI is taken in account the above mentioned ranking modifies as follows: the more resilience process is the FTCDC that is followed by the DQB and SQF and the last is the Conv. Dir. In point of view of the RGAno that indicates the interactions between the control loops of the distillation system the ranking is totally different: the Conv. Dir. shows the less interactions followed by the DQB, FTCDC, SQF. **Table 12** shows that the ranking of the distillation systems in controllability point of view can be confusing if the controllability indices are taken account individually.

Table 12 Ranking of the distillation systems based on individual controllability indices

Ranking	Controllability indices		
	CN	MRI	RGAno
I	DQB	FTCDC	Conv. Dir.
II	SQF	DQB	DQB
III	FTCDC	SQF	FTCDC
IV	Conv. Dir.	Conv. Dir.	SQF

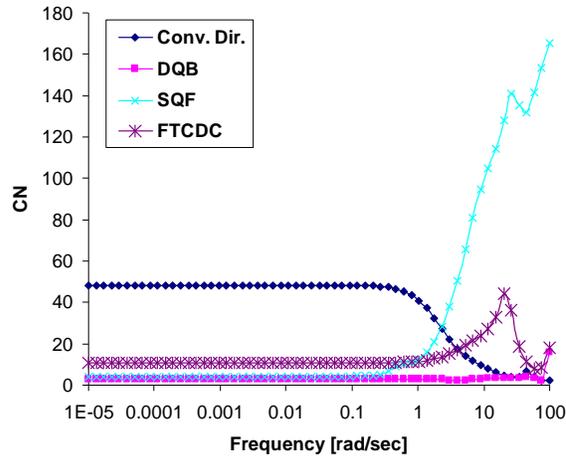


Figure 31 Condition number in function of frequency.

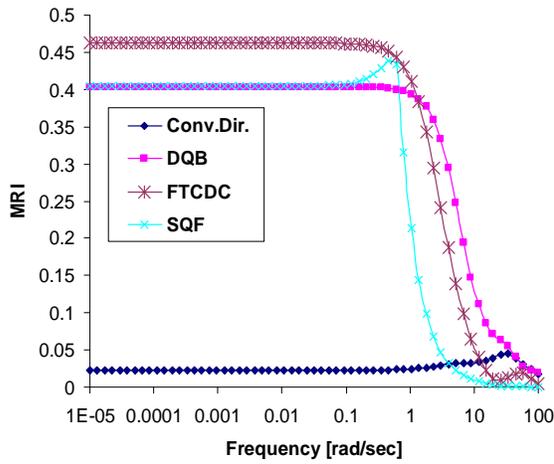


Figure 32 Morari resiliency index in function of frequency.

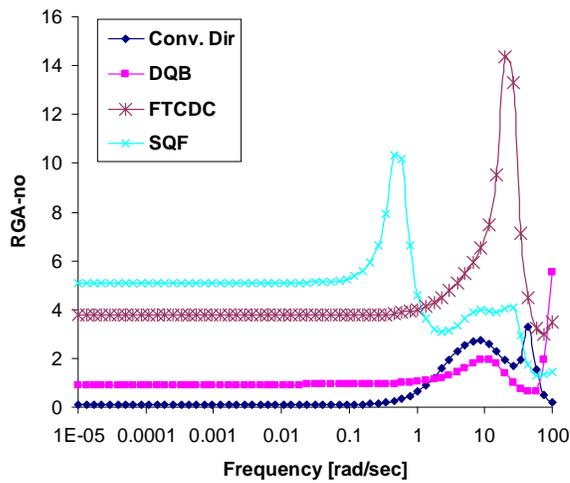


Figure 33 RGA number in function of frequency.

In order to help the decision of the control designer the desirability function is applied. **Figure 34** indicates that the DQB has the best control properties taking into account the three indices, simultaneously.

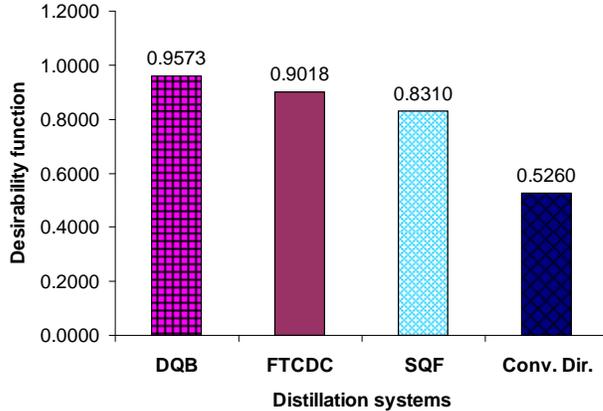


Figure 34 Desirability function values for the studied distillation systems.

The proposed controllability analysis makes it easy to select the best operable distillation systems among the studied ones. Closed loop simulations verify the controllability analysis. The verification consist of load rejection analysis that is carried out by applying different disturbances on the distillation systems with closed-loop control structures.

The closed loop simulations are executed for two types of disturbances: step change in the feed flow rate (from 100 kmol/h to 101 kmol/h) and feed composition (from 0.3300/0.3400/0.3300 to 0.3333/0.3434/0.3233). The PI controllers are tuned with the Ziegler-Nichols method using the automatic tuning tool of Aspen Dynamics in decentralized control structure to maintain the three product compositions at the set point. The quality of the control for different cases is compared based on the integral absolute error (IAE). The responses for the feed flow rate disturbances are shown in Figure 35 - 36. The set point of the composition controller is 0.95 [kmol/kmol] that means the desirable mole fraction of the key component in the three different product stream. Figure 35 shows that the feed flow rate disturbance applied at 5 h is eliminated within 2 hours and the controller placed on the hexane product flow produces the highest overshoot. The dynamic behaviour of the distillation systems during the load rejection analysis is evaluated based on IAE.

$$IAE = \int_0^{\infty} |e(t)| dt \quad (27)$$

The IAE measured during the responses on the feed flow rate is presented in the **Table 13**. As the table shows the best dynamic behaviour has the DQB that is followed by the FTCDC, SQF, and Conv. Dir.

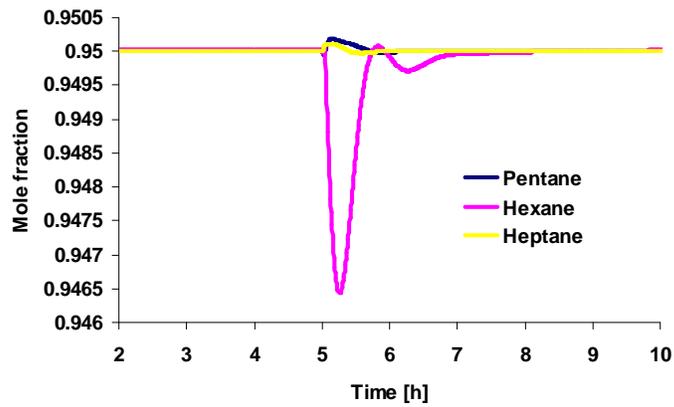


Figure 35 Product composition of DQB after step change in feed flow rate.

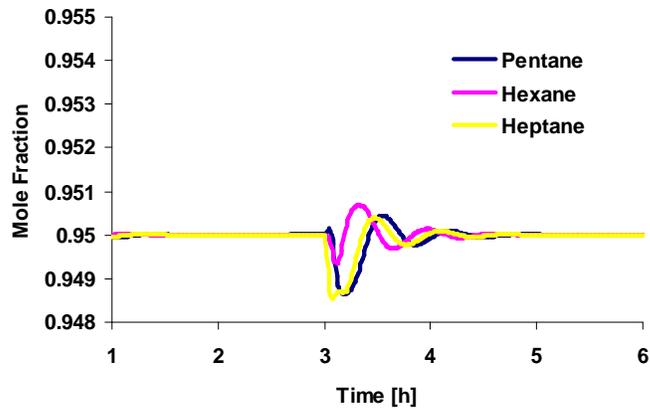


Figure 36 Product composition of FTCDC after step change in feed flow rate.

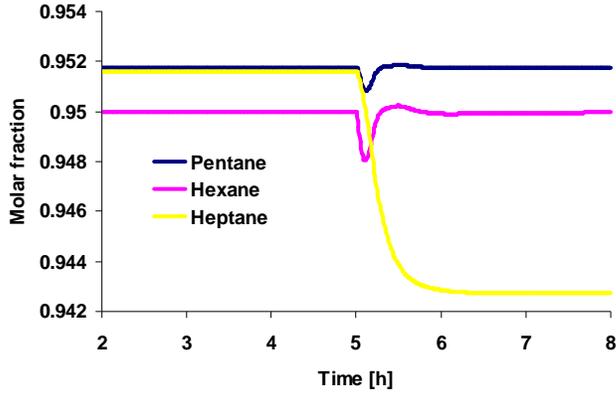


Figure 37 Product composition of SQF after step change in feed flow rate.

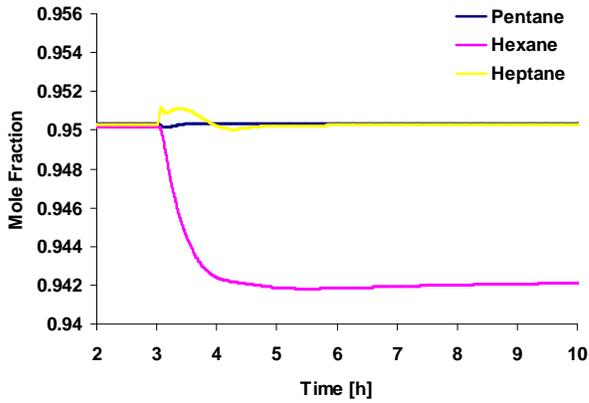


Figure 38 Product composition of Conv. Dir. after step change in feed flow rate.

Table 13 IAE values in the case of feed flow step disturbance

IAE values of product streams	DQB	FTCDC	SQF	Conv. Dir.
Pentane	7.41E-05	1.14E-03	1.92E-04	1.35E-04
Hexane	1.54E-03	4.57E-04	1.42E-06	5.68E-02
Heptane	3.74E-05	7.72E-04	3.51E-02	1.07E-03
Average	5.49E-04	7.88E-04	1.18E-02	1.93E-02
Ranking	I	II	III	IV

The responses for the feed composition disturbances are shown in Figure 39 – 40. Based on the composition disturbance responses the rank of the distillation systems does not change.

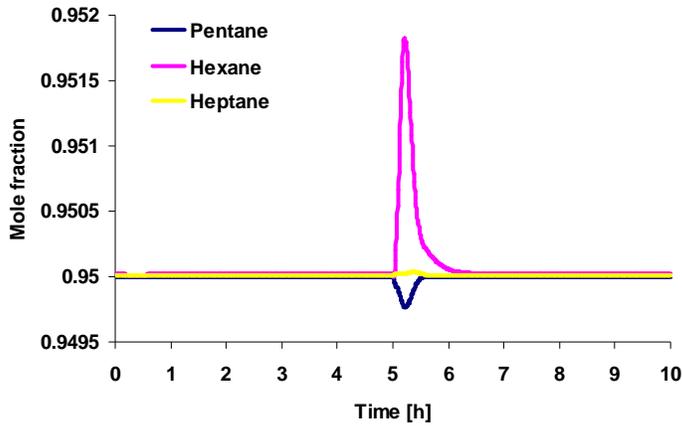


Figure 39 Product composition of DQB after step change in feed composition.

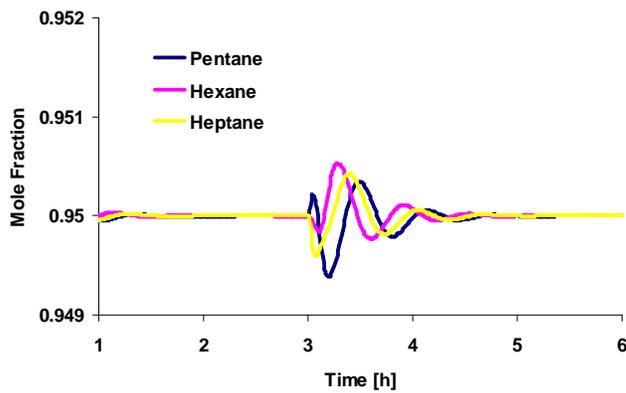


Figure 40 Product composition of FTCDC after step change in feed composition.

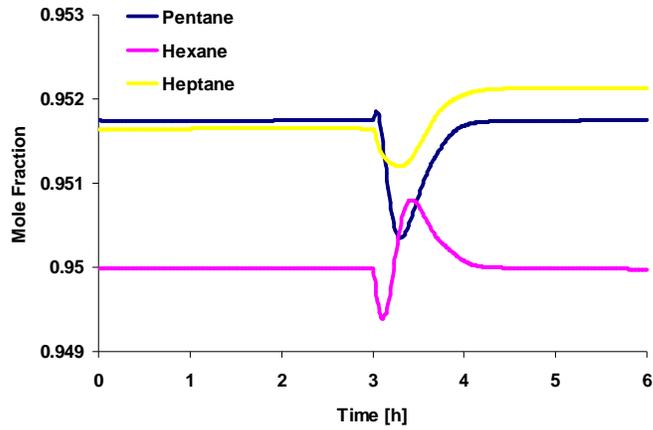


Figure 41 Product composition of SQF after step change in feed composition.

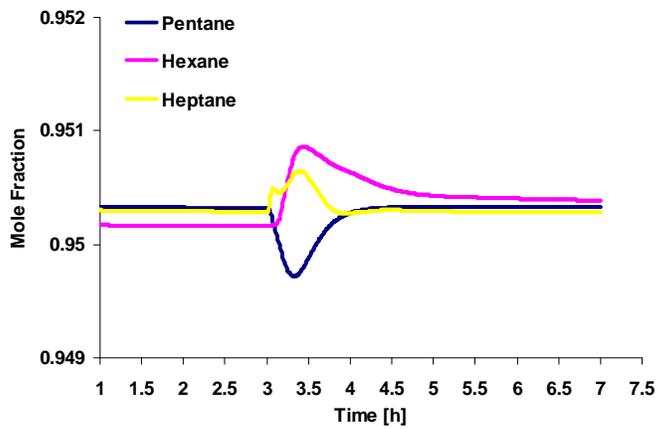


Figure 42 Product composition of Conv. Dir. after step change in feed composition.

Table 14 IAE values in the case of feed composition step disturbance

IAE values of product streams	DQB	FTCDC	SQF	Conv. Dir.
Pentane	1.31E-04	9.10E-04	6.33E-04	3.62E-04
Hexane	2.77E-04	3.40E-04	4.34E-04	1.50E-03
Heptane	1.71E-05	5.19E-04	1.26E-03	4.87E-04
Average	1.42E-04	5.90E-04	7.75E-04	7.83E-04
Ranking	I	II	III	IV

6.3 Conclusion

Chapter 6 proposes a simple controllability analysis that is applied on the studied distillation systems. The controllability analysis investigates the control features of the distillation systems in frequency domain and compares them based on their control properties.

The results of the comparative study of the different distillation systems from controllability point of view show that the direct sequence with backward heat integration (DQB) is the best choice. The second best is the FTCDC and it is followed by the SQF. However, the conventional direct distillation sequence is considered a simple configuration it has the worst control properties. This result can be found odd but it is in correspondence with the results of Alatiqi and Luyben⁵⁶. They compare the control properties of the conventional direct sequence with a thermally coupled distillation system and they find that the conventional sequence presents worst control properties during the controllability analysis and closed loop simulations as well.

The controllability analysis proposed in my thesis is a simple way to evaluate different distillation systems in order to select the easiest operable one. The analysis requires the calculation of the transfer matrices of the investigated distillation systems that is subject to SVD. Based on the calculated singular values the controllability indices can be defined in the frequency domain. These controllability indices are aggregated with the desirability function in order to simplify the decision which system is the easiest to control.

The proposed method is verified with closed-loop simulations and the results correspond with the previous controllability analysis. The application of the controllability analysis sustains that the method is simple and fast, thus it can be used in the early stage of the design procedure.

Chapter 7 Major new results

Thesis 1

1. a.) I proposed an evaluation methodology for distillation systems that helps the engineer at the process design step. The methodology has three levels, which guide the designer in the problem definition, multicriteria evaluation, and ranking of the process design alternatives. The methodology considers the exergy, economic, and emission criteria in order to find the most adequate process design alternative.

I tested the methodology on energy-integrated distillation systems. Theoretically, this methodology can be used on any kind of energy consuming processes in order to evaluate them from exergetic, economic, and emission points of view.

1. b.) First in this research topic, I applied the so called desirability function to rank the process alternatives. For this purpose I elaborated a summarized indicator on the basis of the desirability function to help the choice of the most adequate process alternative for the specific separation task.

Thesis 2

I determined with complex evaluation based on my methodology presented in Thesis 1 that the direct sequence with backward heat-integration (DQB) is the best applicable energy-integrated distillation system in the case of the zeotropic ternary mixture separation since it shows the features in a wide and flexible range. For the sake of the comparison beside of the DQB, I investigated the fully thermally coupled distillation column (FTCDC), and sloppy distillation system with forward heat-integration (SQF), and compared to the conventional direct scheme. I applied exergy analysis, economic study, GHG emission estimation, and investigated the controllability properties. The results show that the DQB is the best process alternative in every issue.

Thesis 3

I determined that the energy integration principles, which were elaborated on ternary hydrocarbon mixtures, are applicable on polar binary mixtures as well. I made a process improvement for the backward heat-integrated distillation system of N, N-dimethylformamid – water separation in industrial scale. My retrofit design study shows that the required capacity increase can be attained by adding an existing distillation column with the replacement of its internals with a new structural packing. With my design the capacity of the DMF – water separation system could be increased by 42.8 %. The energy requirement of the proposed heat-integrated separation system is 35 % of the non-integrated one.

Thesis 4

I elaborated a controllability analysis methodology, which is a simple way to evaluate different process design alternatives in order to select the easiest controllable one. The analysis is based on the state-space representation of the systems investigated. The transfer matrix is subject to singular value decomposition in order to determine the frequency dependent controllability indices, which are summarized with the desirability function. I introduced and successfully applied also for the evaluation of process design alternatives (Thesis 1).

I tested the proposed controllability analysis on energy-integrated distillation systems and I verified the results with load rejection analysis. The results of these analyses are in agreement with the results obtained with the application of the frequency dependent controllability indices. Consequently, I determined that the proposed controllability analysis can be used instead of the tedious and time consuming load rejection analysis. The application of this controllability analysis sustains that the method is simple and fast, thus it can be used in the early stage of the design procedure.

List of Publications

Papers published in refereed journals

1. **Hajnalka Kencse**, József Manczinger, Zsolt Szitkai, Péter Mizsey: Retrofit Design of an Energy Integrated Distillation System, *Periodica Polytechnica, Chemical Engineering*; 51/1, **2007**, 11-16.
2. **Hajnalka Kencse**, Péter Mizsey: Comparative Study of Energy-Integrated Distillation Systems Based on Exergy Analysis and Greenhouse Gas Emissions, *Revista de Chimie*; 60, no. 10 / **2009**, IF=0.389.
3. **Hajnalka Kencse**, Peter Mizsey: Methodology for the Design and Evaluation of Distillation Systems: Exergy Analysis, Economic Features and GHG Emissions, *AIChE Journal*, early view online, **2009**, IF=1.883

Partly related publication

4. Levente L. Simon, **Hajnalka Kencse**, Konrad Hungerbuhler: Optimal rectification column, reboiler vessel, connection pipe selection and optimal control of batch distillation considering hydraulic limitations, *Chemical Engineering and Processing: Process Intensification*, Volume 48, Issue 4, April **2009**, Pages 938-949, IF=1.518.

Conference proceedings

1. **Hajnalka Kencse**, Máté Gábor, Péter Mizsey: Energiaintegrált desztillációs rendszerek modellezése, *Műszaki Kémiai Napok '05*, **2005**, pp 188, ISBN 9639495719, Veszprém, Hungary.
2. Máté Gábor, **Hajnalka Kencse**, Péter Mizsey.: Energiaintegrált desztilláló rendszerek vizsgálata, *Műszaki Kémiai Napok '06*, **2006**, pp 268 Veszprém, Hungary.
3. **Hajnalka Kencse**, Máté Gábor, Péter Mizsey: Comprehensive Investigation of Energy-Integrated Distillation, *17th International Congress of Chemical and Process Engineering*, **2006**, pp 346, ISBN 8086059456, Praha, Czech Republic.
4. **Hajnalka Kencse**, Péter Mizsey: Comprehensive Process Investigation Methodology for Energy-Integrated Distillation, *17th European Symposium on Computer Aided Process Engineering*, **2007**, pp 883, ISBN 9780444531575, Bucharest, Romania.
5. **Hajnalka Kencse**, Péter Mizsey: The Impact of Energy-Integration on carbon dioxide emissions, *Permea 2007, Membrane Science and Technology Conference of Visegrad Countries*, **2007**, pp 265, ISBN 9789639319691, Siófok, Hungary.
6. **Hajnalka Kencse**, Péter Mizsey: Investigation of Exergy Loss and CO₂e Emission for Energy-Integrated Distillation Systems, *35th International Conference of SSCHE*, **2008**, pp 49, ISBN 9788022729031, Tatranské Matliare, Slovakia.
7. **Hajnalka Kencse**, Péter Mizsey: Investigation of CO₂e Emission for Energy-Integrated Distillation Systems, *INTERFACES '08 Sustainable development in petroleum refining and petrochemistry*, **2008**, pp 81, 9789639319868, Sopron, Hungary.

Oral lectures and presentations

1. **Hajnalka Kencse**, Máté Gábor, Péter Mizsey: Energiaintegrált desztillációs rendszerek modellezése, *Műszaki Kémiai Napok '05*, **2005**, Veszprém, Hungary.
2. **Hajnalka Kencse**, Máté Gábor, Péter Mizsey: Comprehensive Investigation of Energy-Integrated Distillation, *17th International Congress of Chemical and Process Engineering*, **2006**, Praha, Czech Republic.
3. **Hajnalka Kencse**, Máté Gábor, Péter Mizsey: Az energiaintegrált desztilláció átfogó vizsgálata, *BUTE, Doctorandus Conference at Faculty of Chemical Technology and Biotechnolog*, **2006**, Budapest, Hungary.
4. **Hajnalka Kencse**, Péter Mizsey: Összetett vizsgálati módszer energiaintegrált desztilláció tanulmányozására, *BUTE, Doctorandus Conference at Faculty of Chemical Technology and Biotechnology*, **2007**, Budapest, Hungary.
5. **Hajnalka Kencse**, Péter Mizsey: Vizsgálati módszer energiaintegrált desztilláció tanulmányozására, *Annual meeting of Richter Gedeon Centenary Foundation*, **2007**, Budapest, Hungary.
6. **Hajnalka Kencse**, Péter Mizsey: Investigation of Exergy Loss and CO₂e Emission for Energy-Integrated Distillation Systems, *35th International Conference of SSCHE*, **2008**, Tatranské Matliare, Slovakia.
7. **Hajnalka Kencse**, Péter Mizsey: Investigation of CO₂e Emission for Energy-Integrated Distillation Systems, *INTERFACES '08 Sustainable development in petroleum refining and petrochemistry*, **2008**, Sopron, Hungary.
8. **Hajnalka Kencse**, Péter Mizsey: Desztillációs rendszerek komplex vizsgálata, *Műveleti Munkabizottság Ülés*, **2008**, Budapest, Hungary.
9. Péter Mizsey, **Hajnalka Kencse**: Desztillációs rendszerek komplex vizsgálata: energia, exergia, szabályozás, környezet, *Hungarian Society for Industrial Ecology meeting*, **2009**, Budapest, Hungary.

Posters

1. **Hajnalka Kencse**, Péter Mizsey: Comprehensive Process Investigation Methodology for Energy-Integrated Distillation, *17th European Symposium on Computer Aided Process Engineering*, **2007**, Bucharest, Romania.
2. **Hajnalka Kencse**, Péter Mizsey: The Impact of Energy-Integration on carbon dioxide emissions, *Permea 2007, Membrane Science and Technology Conference of Visegrad Countries*, **2007**, Siófok, Hungary.

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Nomenclature

Latin symbols

A	The most volatile component of the ternary mixture
a	Fitted parameter
A_{HT}	Heat transfer area, [m ²]
B	Middle component of the ternary mixture
B	bottom product rate of the distillation column, (kmol/h)
b	Fitted parameter
C	The heaviest component of the ternary mixture
CN	Condition number
CO _{2e}	Carbon dioxide equivalent, [kg]
c_p	Specific heat capacity, [kJ/kg K]
d	Individual desirability value
D	Distillate flow rate of the distillation column, (kmol/h)
D_{col}	Column diameter, [m]
D_{fct}	Desirability function
DMF	N,N-dimethylformamid
DQB	Direct distillation sequence with backward heat integration
Ex	Specific exergy, [kJ/kmol]
Ex _{loss}	Lost exergy rate, [kW]
F_c	Correction factor
FTCDC	Fully thermally coupled distillation column

GWP	Global warming potential
H	Molar enthalpy, [kJ/kmol]
H _C	Column height, [m]
HETP	Height equivalent to a theoretical plate
H _T	Tray stack height, [m]
IAE	Integral absolute error
L	Reflux rate of the distillation column, (kmol/h)
L ₁₂	Liquid flow rate from column 1 to column 2, [kmol/h]
L ₂₁	Liquid flow rate from column 2 to column 1, [kmol/h]
M&S	Marshall and Swift index
m	Weight factor
M	Maximum vapour flow rate, [kg/h]
MRI	Morari resiliency index
n	Mole flow, [kmol/h]
Q	Heat duty of the column's reboiler, (kW)
Q _{cond}	Heat duty of the condenser, [kW]
Q _{reb}	Heat duty of the reboiler, [kW]
r	Latent evaporation heat, [kJ/kg]
RGA	Relative gain array
RGAno	Relative gain array number
S	Molar entropy, [kJ/kmol K]
SI	Separation Index
SQF	Sloppy distillation system with forward heat-integration

SVD	Singular value decomposition
T_0	Ambient temperature, [K]
T_{cond}	Cooling water temperature, [K]
T_{ol}	Time constant, [sec]
T_{reb}	Heating steam temperature, [K]
TAC	Total annual cost, [\$/year]
V_{12}	Vapour flow rate column 1 to column 2, [kmol/h]
V_{21}	Vapour flow rate from column 2 to column 1, [kmol/h]
v_m	Maximum specific vapour velocity, [m/s]
W_{SEP}	Work of separation, [kW]

Greek letters

α_i	Volatility of component i
α_{ij}	Relative volatility of components i, j
β	Optimal fractional recovery of the middle component
ΔS_{irr}	Entropy production, [kJ/h K]
ΔT_{med}	Logarithmic mean temperature difference
η	Thermodynamic efficiency
ρ	Maximum vapour density, [kg/m ³]
ω_{crit}	Critical frequency, [rad/sec]

List of figures

Figure 1	General feedback control loop block diagram.	17
Figure 2	Binary distillation column with control loops.....	18
Figure 3	Direct distillation sequence with backward heat integration (DQB).	25
Figure 4	Fully thermally coupled distillation column (FTCDC).....	26
Figure 5	Sloppy distillation system with forward heat-integration (SQF).	27
Figure 6	Conventional direct distillation scheme (Conv. Dir.).	27
Figure 7	Flow diagram of the complex evaluation methodology of distillation systems.....	30
Figure 8	Exergy loss in function of the separation index.	39
Figure 9	Thermodynamic efficiency in function of the separation index.	39
Figure 10	Exergy loss of the two distillation columns in the case of mixture with SI=1.03.....	40
Figure 11	Heat demand of the distillation systems in function of the separation index.....	41
Figure 12	TAC vs. SI when the required product purity is 90%.....	42
Figure 13	TAC vs. SI when the required product purity is 95%.....	43
Figure 14	TAC vs. SI when the required product purity is 99%.....	44
Figure 15	CO ₂ e emission of the studied distillation systems at different product purities in case of mixture with SI=1.03, with natural gas as fossil fuel.	46
Figure 16	CO ₂ e emission of fossil fired distillation structures, the product purity is 95%, mixture with SI=1.03.	46
Figure 17	CO ₂ e emission of the distillation systems, in the case of different ternary mixtures. The required product purity is 95% and with natural gas as fossil fuel.	47
Figure 18	CO ₂ e relative emission saving correlate to the conventional direct distillation scheme.	47
Figure 19	D _{ft} vs. SI for the studied distillation systems.	48
Figure 20	The original DMF-water separation system with backward heat integration.	53
Figure 21	Simulation of the original DMF-water separation system.	54
Figure 22	Internal vapour and liquid flows in the vacuum column (column I).....	57
Figure 23	Internal vapour and liquid flows in the atmospheric column (column II).....	57
Figure 24	Separation efficiency of Sulzer packings at 200 mmHg.....	59
Figure 25	Separation efficiency of packings at 720 mmHg.	61
Figure 26	Heat-integrated retrofit design for the separation of 20 tons/h DMF-water mixture.	62
Figure 27	DQB indicating its controlled and manipulated variables.	69
Figure 28	FTCDC indicating its controlled and manipulated variables.....	70
Figure 29	SQF indicating its controlled and manipulated variables.	70
Figure 30	Conv. Dir. indicating its controlled and manipulated variables.....	70
Figure 31	Condition number in function of frequency.....	72
Figure 32	Morari resiliency index in function of frequency.	72
Figure 33	RGA number in function of frequency.	72
Figure 34	Desirability function values for the studied distillation systems.....	73
Figure 35	Product composition of DQB after step change in feed flow rate.	74
Figure 36	Product composition of FTCDC after step change in feed flow rate.....	74
Figure 37	Product composition of SQF after step change in feed flow rate.....	75
Figure 38	Product composition of Conv. Dir. after step change in feed flow rate.....	75
Figure 39	Product composition of DQB after step change in feed composition.	76
Figure 40	Product composition of FTCDC after step change in feed composition.....	76
Figure 41	Product composition of SQF after step change in feed composition.	77
Figure 42	Product composition of Conv. Dir. after step change in feed composition.....	77

List of tables

Table 1	Ternary mixtures studied	28
Table 2	Expected product purities	28
Table 3	Separation task for DQB case study.	28
Table 4	Summary of the data required for the application of the evaluation methodology	31
Table 5	Global warming potentials of different greenhouse gases	35
Table 6	Specifications of the columns of the existing separation system	55
Table 7	Reboiler data of the vacuum columns.....	56
Table 8	Condenser data of the atmospheric column	56
Table 9	Energy requirement for the recovery of DMF	63
Table 10	Energy requirement for the recovery of 1 kg DMF	63
Table 11	Selected manipulated variable pairings	69
Table 12	Ranking of the distillation systems based on individual controllability indices	71
Table 13	IAE values in the case of feed flow step disturbance.....	75
Table 14	IAE values in the case of feed composition step disturbance	77

Appendix A

Equations for the economic study

The equations used for capital and operating cost calculations are the following.

The installed cost of column shell is calculated using equation A.1:

$$\text{Installed cost of column shell, \$} = \left(\frac{M \& S}{280} \right) 101.9 D_{col}^{1.066} H_C^{0.802} (2.18 + F_c) \quad (\text{A.1})$$

where the value of correction factor F_c depends on the pressure and shell material of the column and it ranges between 3-10. The chosen shell material is carbon steel.

M&S stands for the Marshall and Swift cost index published in Chemical Engineering⁵⁰. The M&S updates the equipment costs of process industry to the present time. This index is used to give a general estimate, but can not take into account all factors that affect the equipment prices.

Installed cost of tower internals is calculated using column diameter and the tray stack height (H_t , [m]). The tray type is bubble cap.

$$\text{Installed cost of tower internals, \$} = \left(\frac{M \& S}{280} \right) 4.7 D_{col}^{1.55} H_t F_c \quad (\text{A.2})$$

where the correction factor's (F_c) value varies depending on tray spacing, type and material.

Installed cost of reboiler or condenser is estimated with installed cost of heat exchanger.

$$\text{Installed cost of reboiler, condenser, \$} = \left(\frac{M \& S}{280} \right) 101.1 A_{HT}^{0.65} (2.29 + F_c) \quad (\text{A.3})$$

where A_{HT} [m²] is the heat transfer area. The value of correction factor (F_c) depends on the type of heat exchanger and the chosen value is 5.

Cooling water cost is calculated per year and it is the product of water price [\$/t] and the mass flow rate of cooling water [t/h]. The required water mass flow is calculated with equation A.4:

$$\text{Mass flow rate of cooling water, [kg/s]} = \frac{Q_{cond}}{\Delta T_{med} \times c_p} \quad (\text{A.4})$$

where c_p [kJ/kg K] is specific heat capacity of cooling water.

Steam cost is also calculated per year and it is the product of the price of steam [\$/t] and the steam flow rate [t/h]. Calculating steam costs: the heat duty of the reboiler is known and the required steam flow rate is calculated using equation A.5:

$$\text{Steam flow, [kg/s]} = \frac{Q_{reb}}{r} \quad (\text{A.5})$$

where r [kJ/kg] is the latent evaporation heat of water.

The value of Marshall and Swift index, used in the dissertation is: M&S = 1164.3.

The cost of steam: 18.1 \$/t and the cost of cooling water: 0.042 \$/t.

Appendix B

Investigated distillation system design

Table B.1. Investigated distillation system design and results in the case of isopentane-pentane-hexane separation (SI=0.47), product purity 95%

Description	DQB		SQF		FTCDC		Conv. Dir.	
	Col.1	Col.2	Col.1	Col.2	Col.1	Col.2	Col.1	Col.2
Pressure [bar]	1	6	7	1.2	1	1	1	1
Diameter [m]	1.85	1.45	1.4	1.7	1.5	2.1	1.63	0.85
Reflux ratio	9.9	1.04	0.64	8	0.66	11	6.35	1.26
Nr. stages	80	10	30	50	7	83	60	20
Feed stage	36	6	10	45	5	-	25	10
Reboiler duty [kW]	-	2212.2	2055.6	-	-	2502.1	1853.7	562
Condenser duty [kW]	1848.8	-	-	1916.0	-	2110.3	1768.0	546.0
W _{sep} [kW]	45.2	6.14	130.15	-77.11	-85.15	135.85	42.5	10.17
Exergy loss [kW]	348.1	317.1	246	386	71.2	691.1	599.1	184.4
TAC ×10 ³ [\$ /year]	7.03165		7.19357		9.79364		8.223912	
GHG emission (fuel: natural gas)	1113.8		907.1		1284.4		1334.6	

Table B.2. Investigated distillation system design and results in the case of **pentane- hexane- heptane** separation (**SI=1.03**), product purity 95%

Description	DQB		SQF		FTCDC		Conv. Dir.	
	Col.1	Col.2	Col.1	Col.2	Col.1	Col.2	Col.1	Col.2
Pressure [bar]	1	5	7	1.2	1	1	2	1
Diameter [m]	1.01	1.06	1.15	1.07	1.17	1.42	0.9	0.97
Reflux ratio	1.4	0.65	0.58	2.4	0.56	3.25	1.15	2
Nr. stages	40	40	25	70	17	80	40	40
Feed stage	22	18	12	55	10	-	20	15
Reboiler duty [kW]		995.3	1228.2			1192.3	603.2	905.9
Condenser duty [kW]	599.2			806.2		1072.1	512.5	770.7
W_{sep} [kW]	49.3	-3.6	171	-130	-28.7	76.4	43.6	-3.1
Exergy loss [kW]	119.4	182.3	156	172	36.8	332	165.1	316.6
TAC $\times 10^3$ [\$/year]	3.1984		4.18078		4.35044		5.262007	
GHG emission (fuel: natural gas)	367.2		462.5		552.9		613.1	

Table B.3. Investigated distillation system design and results in the case of butane- isopentane- pentane separation (SI=1.74), product purity 95%

Description	DQB		SQF		FTCDC		Conv. Dir.	
	Col.1	Col.2	Col.1	Col.2	Col.1	Col.2	Col.1	Col.2
Pressure [bar]	1	3	7	1	1	1.5	2	2
Diameter [m]	1.43	1.40	1.54	1.89	1.27	2.06	1.02	1.5
Reflux ratio	5.71	0.86	0.87	9.7	0.68	13	3	7.35
Nr. stages	16	90	10	70	15	80	20	60
Feed stage	6	50	5	53	8	-	11	35
Reboiler duty [kW]		1815	2090.1			3143.9	973.0	2069.0
Condenser duty [kW]	1776.1			2174.6		3049	937	2158
W_{sep} [kW]	33.8	16.27	60.69	-10.66	62.09	111.97	38.58	12.95
Exergy loss [kW]	100.8	492	431.6	252.7	62	948.9	298.4	703.4
TAC $\times 10^3$ [\$/year]	5.45076		7.55698		11.04038		10.27356	
GHG emission (fuel: natural gas)	987.4		991.4		1254.3		1294.4	

Declaration

I declare that this thesis was done by me and all of the used sources are referred at the end on the thesis.

The research work reported in this thesis has been carried out under the supervision of Prof. Dr Peter Mizsey, Head of Department of Chemical and Environmental Process Engineering at Budapest University of Technology and Economics.

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this, or any other university, or other institute.

Hajnalka Kencse

Budapest, August 12th, 2009.

NYILATKOZAT

Alulírott ...Kencse Hajnalka....kijelentem, hogy ezt a doktori értekezést magam készítettem és abban csak a megadott forrásokat használtam fel. Minden olyan részt, amelyet szó szerint, vagy azonos tartalomban, de átfogalmazva más forrásból átvettem, egyértelmően, a forrás megadásával megjelöltem.

Kencse Hajnalka

Budapest, 2009. augusztus 12.....