Budapest University of Technology and Economics
Faculty of Chemical Technology and Biotechnology
George Oláh Doctoral School

Complex Energetic and Process Control Investigation of Distillation Systems

PhD Thesis

by
Máté Haragovics

Under the supervision of
Dr. Péter Mizsey

Department of Chemical and Environmental Process Engineering

Budapest

2014

Acknowledgements

I would like to express my greatest gratitude to Prof. Dr. Péter Mizsey for his guidance and support during the time spent under his supervision.

I am also grateful for MOL Public Limited Company, TÁMOP-4.2.2.A-11/1/KONV-2012-0072 project, and Varga József Foundation for their financial support of my research, as well as for co-workers of MOL PLC. for their helpful attitude.

Herewith, I also would like to thank all the colleagues at the Department of Chemical and Environmental Process Engineering, for helping me in technical, scientific, and intellectual questions; and for providing a friendly atmosphere at the department. I would like to gratefully acknowledge the help of Dr. Hajnalka Kencse and Dr. Marcell Horváth, who have helped me with my first steps on the rocky road of doing research.

I am forever indebt to my parents, my family, and friends; that they encouraged and supported my studies and helped me getting through the difficulties I came up with. This thesis would not have been possible without this supporting milieu.

Abstract

In this thesis different problems are investigated that may arise in connection with the design and operation of distillation columns. During my studies the purpose was to add more value to the existing methods of design while keeping their simplicity, which unquestionably helped them to be widely utilised in the practice of process design. With the application of the exponentially growing computational power and high quality software available, it is now possible to include more complex evaluations in the design process, and to connect the software and share large amounts of data between them. The newer, more complex processes, however, shall not appear any more complex to the user than previously.

The first problem, this thesis discusses, is a new applicability of exergy analysis. In the investigation quaternary liquid mixtures are separated with five different distillation systems satisfying two purity specifications: a sloppy and a sharp separation. The Exergy Analysis is used with two different boundaries to evaluate a distillation system as a separete plant, and the core process that can be understood as a plant that is totally and optimally integrated to a Ideal Background Heat Cascade, or Ideal Total Site. It is shown on these series of examples that the the Exergy Analysis is a powerful tool to assess flexibility of systems. The first case is, when heat transfer to or from the background processes can occur on any temperatures and can any volume of heat can be transferred. This case corresponds to the ideal case of Total Site Integration. The other case of Exergy Analysis is, when there is one unified heat source an one unified cooling utility for all the equipment, representing an isolated distillation plant. For example, the Conventional Direct Sequence distillation scheme performs well in an Ideal Total Site environment, where integration possibilities are infinite, but has a lesser performance if regarded as an individual plant. This approach also helps to design distillation structures that are flexible, yet energy efficient, as required by lean manufacturing principles.

As Exergy Analysis uses the ambient temperature for calculations, that may vary even on the same site throughout a year, it is important to investigate the effect of ambient temperature on the efficiencies and ranks of the distillation systems. The results show that regarding efficiencies the results do not change much, however in some cases some systems change places. In the core case, however the ambient temperature has no effect on ranks by thermodynamic efficiency.

Finally, a Process Control study is presented. In this study the frequency domain investigations are tested if they are eligible to replace time consuming

Time Domain simulations. The performance of control structures are evaluated by using Control Performance Indicators, namely MRI, CN and RGAno. These indicators are widely used in steady-state and dynamic calculations also; however, each indicator aims to benchmark a different property. The idea is to aggregate these different indicators with Desirability Function for the reason that they often deliver contradictory results alone. Simulations cover three binary mixtures and five control structures for a Direct Sequence distillation scheme. Time Domain simulations are also carried out to give a reference of the realistic performance of the control structures.

The results in Frequency Domain show several similarities. Ranks according to different indicators vary, but in these cases desirability function can be used easily. However, comparison of Time Domain and Frequency Domain results, it is clearly visible that Frequency Domain does not fulfil the requirements. The worst controllable structures according to Time Domain results have the best results in Frequency Domain, and the worse control structure in Frequency Domain have good ranks in Time Domain. Neither the aggregated, nor the individual indicators show similarities with Time Domain results. Thus, it can be concluded that despite its successful application to choose best controllable distillation scheme, the method is not eligible for control structure design of a distillation scheme. The designer has to stick to time domain simulations.

Contents

Chapter 1

Introduction and Topic Choice

> "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

1.1 Motivation

In this chapter the basic thoughts behind my work are presented concisely, motivations of my work are summarized and the approach to the research is described. Chemical engineering has great industrial importance all over the world. Production, separation and purification of materials, chemicals and compounds is needed for everyday life. Technologies nowadays need precise composition of materials, which we can be achieved by adequate separation processes. A large portion of separation industry aims the liquid mixtures. Several kinds of technologies have been developed during the last decades, but they could not reach the popularity of distillation, one of the oldest separation technique for separating liquid mixtures. Still being the flagship separation technology in the hydrocarbon industry and being commonly applied in other industries that use liquid material separation; distillation has an important role in the present, and will remain widely utilised for a long time in the future. This encourages researchers to investigate the distillation process despite its maturity.

The volume of liquid mixtures separated by distillation is extremely high, mainly due to petrol refining. Large volumes assume large savings even on small improvements, and regarding these circumstances distillation is still investigated in many fields. Investigations focus on every possible aspects of distillation from energetic questions to process control. The timelessness of the need for distillation implies that the design of new plants is a very important task as

well as to retrofit existing ones, or improve operation. Distillation columns may be operated for decades, sometimes 40–50 years or even more. The long life cycle also requires that special care must be taken in the design process. Many different factors have to be taken into account, and it is also important to be future-proof on a certain level.

Chemical process design is a complex process engineering problem that involves synthesis, analysis, optimization activities, and the evaluation of the design alternatives. In the case of a new design, the designer has a very large number of possible solutions, which are first filtered by the most common rules of thumb and by engineering tools. The remaining alternatives then have to be investigated accurately. The first step is very important, in order to save work in the second step, and not to miss promising solutions. The more viewpoints are taken into account, the more possible alternatives survive the first filter, as there is a higher chance that a system is advantageous from one of the viewpoints. Therefore it is important to choose the right tools that provide fast and reliable filtering, and ensure a more versatile solution than the economic evaluation itself, that was used before. Technically: the design process is an optimisation, which should be extended to more dimensions than it uses.

Operating large plants and complex systems have a huge effect on the environment. In the last decade a paradigm-shift has been made from end-of-the-pipe cleaning technologies towards design processes that prefer environmentally-conscious designs. Earlier these systems were evaluated only based on viewpoints that focused on the separation, and regulations (emission, etc.) were satisfied by additional equipment, and often additional investments. The newer paradigm handles the problems before they occur.

Throughout the years another factor helped to alter the design process. The boom of the personal computer market and fast evolution of computational capacities and speeds of computers was followed by the evolution of engineering software. Computer-aided design (CAD) has conquered chemical engineering as well as other fields of engineering. The ability to investigate rigorous models of plants and equipment made it easier, faster, and simpler to involve more aspects in the design process.

The demand for complex design process and the ability to make simulations easier has great potential. In order to help engineers, at the present level of software and computer hardware design process can be at least partly automated; thus, engineers can concentrate on important decisions after the results are calculated. However, an important question remains: which parameters should be regarded as Performance Indicators or benchmarks and should be taken into account during design. Which can be used in general and which should be omit-

ted? In this thesis such indicators are investigated, as well as methods to take these indicators into account.

1.2 The Aims of This Work

With the given circumstances it became possible to investigate more complex design procedures than before. By complex design, we usually mean a bundle of previously existing evaluational and computational methods applied together in some ways.

In this study, my goal is to test and evaluate properties and indicators that may be included in complex design of distillation systems. With properly chosen indicators it is possible to simplify certain parts of the design process, while making it more comprehensive and precise. The result of the complex design is a limited number of alternatives (possibly just one, the most suitable), that should be subjected to further investigations, including more specific properties, and the most detailed design.

To satisfy the needs of simplicity and robustness the simulations have to be as detailed as possible, but without sacrificing the ease and speed. The indicators to be used have to be acquired from these simulations, otherwise there would be no gain compared to present manual methods.

1.3 Approach

The simulations used for this thesis were implemented in Aspen Plus and Aspen Plus Dynamics. Environmental impact assessment is based on data provided by SimaPro software.

Controllability investigations used the Control Design Interface of Aspen Plus Dynamics, and MATLAB for evaluation of state-space matrices. Exergy Analysis and cost have been made in Microsoft Excel, that was connected to Aspen Plus through Visual Basic for Applications and Aspen Custom Modeler.

In this configuration simulations can be modified and run from Excel, and after the simulation is run, data needed for calculations are written back to the spreadsheet. Such software connections greatly improve the efficiency of computer-aided engineering work, while show the advantages of automation of the design process.

Data of energy prices is gathered from Danube Refinery of MOL PLC.

1.4 Overview of the Dissertation

In Chapter 2 a literature review is presented in connection with the investigated topics: exergy analysis, controllability analysis, cost analysis, greenhouse gas emission and indicator aggregation. Previous researches in the investigated topics are summarised, the state of the art is presented.

Chapter 3 shows the problems and possibilities of exergy analysis. Simulations include five distillation schemes, two quaternary mixtures and two levels of separation. A new method of Exergy Analysis and a new direction in design based on lean manufacturing is shown, and additional benefits of Exergy Analysis are presented.

In Chapter 4 the control structure design process is investigated on a single distillation column. Usability of Frequency Domain indices is compared against Time Domain simulations for variable pairing.

Finally, Chapter **??** summarises the major new results of this thesis.

In Appendices A and **??** additional results can be seen with which I did not want to worsen readability.

Chapter 2

Literature Review

2.1 Current Topics of Distillation

Distillation is a widely applied, well-known, mature, and reliable technique. Some industries, like petroleum refining use distillation for most of the separation. However, despite maturity, the weight of the technique in the world's industry still induces scientific investigation in several fields. Regulations and technological improvements challenge existing techniques, and despite the decades spent with research of distillation new fields of application still have been found. Such publications discuss regenerating solvents or processing process wastewater to lower Adsorbable Organically Bound Halogens or Chemical Oxygen Demand (Koczka and Mizsey 2010; Mao et al. 2010; Tóth et al. 2011), or Multi Effect Distillation (Zhao et al. 2011) or even Solar Distillation of olive mill wastewater (Potoglou et al. 2004). These works have proved that distillation can even compete with newer technologies in some cases, and it can solve these problems in a more economic and reliable way.

Most of the researches, however, focus on the improvement of distillation process. More efficient use of energy, heat and energy integration, stable operation and control, and design issues are the most frequent topics.

In an environment with quickly growing energy demands the value of energy also rises rapidly. Due to the large quantities of separated materials, the energy consumption of distillation in the world is very high. As large amount of energy is used in refineries and petrochemical plants, every small improvement yields in great savings. It is not unusual that modifications of processes have a rate of return measured in a few months.

Most of the energy consumption is still covered by fossil energy sources; therefore, consuming energy also means emission of CO_2 and other flue gas compounds into the atmosphere. This is considered to cause greenhouse effect and, at elevated concentrations, global warming. As energy sources are finite, and the primary energy usage of the world rises constantly (Figure 2.1) energetic efficiency becomes more and more important.

Better energy utilisation can be achieved in two possible ways: more efficient technologies have to be used, or efficiency of operation of existing equipment has to be improved. It is not unusual that existing equipment can be improved by refitting columns, or changing column internals. On the other hand the losses not necessarily stem from the equipment or its internals, but the operation mode of the asset.

From technological side more recent papers cover the improvement of heat integrated distillation systems like internally heat integrated distillation column (Gadalla et al. 2007), intensified heat integrated column (Kiran et al. 2012), and

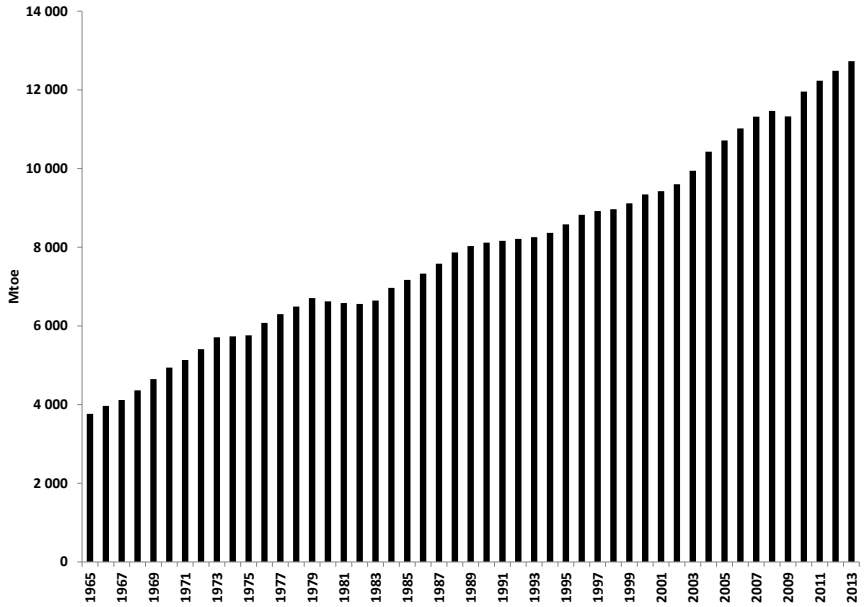


Figure 2.1: World Total Primary Energy Consumption (BP 2014)

totally heat integrated distillation column (Huang et al. 2008).

Complex design has also been investigated in the last decade; which suggests that the need for fast decisions and for simple and easy evaluations is probably higher than ever. Adiche and Vogelpohl (2011), Grossmann et al. (2005), and Wang et al. (2008) discussed automatic methods to design complex distillation structures.

A possible way is to extend these methods to include economic and energetic considerations in order to include points of view that usually affect decisions in economy. Kencse and Mizsey (2010) compared different energy integrated schemes by assessing several factors. They used exergy analysis, GHG emission analysis and economic analysis together. They presented a simple way to aggregate these aspects with the desirability function, and tested it on ternary mixtures.

2.2 Evaluation and Improvement of Energy Efficiency

During design engineers have several tools to evaluate and improve distillation structures from energy efficiency point of view. The most renowned tools are Pinch Analysis and Exergy Analysis.

2.2.1 Pinch Analysis

The idea of Pinch Analysis was first introduced by Linnhoff and Flower (1978) for heat integration. Later the idea was further developed, and published as a handbook for engineers (Linnhoff et al. 1982). The basic idea in Pinch Analysis is to reduce the external heating and cooling utility usage by preferring heat exchange between process streams. The method is aided by visualisation tools like the so-called Composite Curve (CC), and the Grand Composite Curve (GCC). This technique aids optimal utilisation of different quality heats.

Since its initial publication, Pinch Analysis has received great attention, and several contributions have been made. The idea of integration networks has already involved mass transfer networks (El-Halwagi and Manousiouthakis 1989), and is called Mass Pinch. This approach can help to reduce fresh water intake for example (Wang and Smith 1994), or to optimise carbon emission (Tan and Foo 2007). Pinch Analysis has also been successfully applied for properties (Shelley and El-Halwagi 2000), for power (Klemeš et al. 1997) and lately for hybrid power systems (Wan Alwi et al. 2012).

The full history of Pinch Analysis is very accurately summarised in the work of Klemeš and Kravanja (2013).

Pinch technique is a method that collects available heat supply and demand, and visualises it on the Composites Curves and Grand Composite Curves, that show where heat integration possibilities are. It can be applied for plants or even complete sites. The main drawback of Pinch Analysis for our causes is that it does not include all energy types, moreover, for every case new composite curves need to be created. In the case of a larger site it would generate a vast number of charts that have to be evaluated. A solution to extend pinch analysis to include different types of energy is presented in the work of Feng and Zhu (1997), however, the method still uses charts that are difficult to evaluate when a vast amount of possibilities are analysed.

Suphanit et al. (2007) also used Pinch Analysis to detect heat transfer potential in a divided wall column, but used Exergy Analysis alongside with Pinch

Analysis to gather more information to be able to choose the exact plate where heat should be added or not.

2.2.2 Total Site Integration

The more systems or plants are involved in the integration, the more integration possibilities there are. That also means more temperature levels with which a better utilisation of exergy may be possible with better distributed heat transfers. Thus, another expression have to be mentioned here is the Total Site Analysis. Total Site Analysis is an approach that aims to utilise heat at more temperature levels by including several plants and sites in the integration, and provides even more possibilities and availability temperatures than a smaller scale integration. The term was first introduced by Dhole and Linnhoff (1993). They extended the Pinch Technique to a larger scale; Total Site Integration is energy integration between different plants and factories. The method was further developed by Klemeš et al. (1997).

Since the first application of the idea, many publications have been born investigating possibilities of integration between neighbouring plants of many types. Hackl et al. (2011) investigated chemical companies, Matsuda et al. (2012) identified large saving potential in a steel plant, which was considered well integrated before the investigations. Khoshgoftar Manesh et al. (2013) investigated a desalination plant, first by identifying potential for integration, then, in the next step, by a targeting model. Bandyopadhyay et al. (2010) presented a method, that does not remove pockets from individual GCCs in order to increase overall integration of the site.

Modifications of the original concept have also been developed, for example the work of Varbanov et al. (2012), who used process specific minimum temperature difference. Total Site Analysis can also be combined with Exergy Analysis (Hackl and Harvey 2013), as these methods are closely related.

In this work an Ideal Background Heat Cascade is assumed, that ensures zero exergy loss outside the boundaries of a process that is integrated to this heat cascade. It can source and sink any amount of heat at any temperature. A large site can be a feasible version of such a heat cascade: several processes providing several integration possibilities at several temperatures.

2.2.3 Exergy Concept

The idea behind the exergy concept is that the energy content of a material is only valuable until certain parameters reach those of the surrounding environ-

ment.

This way exergy content can be found in heat, chemical energy, kinetic energy, potential energy, or any form of energy that differs from the reference environment. The reference environment for chemical exergy is a reference athmosphere (25 ℃temperature, 1 atm pressure) with the reference concentrations of materials. These concentrations can be seen in Table 2.1.

Molecule	Fraction
N_2	75.67%
O_2	20.35%
H_2O(g)	3.12%
CO_2	0.03%
other gases	0.83%

Table 2.1: Composition of Reference Athmosphere (Moran 2011)

2.2.4 Exergy Analysis

Another powerful engineering tool is Exergy Analysis. Since the energy related crises, processes were optimised for energy consumption, but usually the quality of the energy was not considered. However, different energy types and even energies of the same type generally have different qualities. The difference can be originated from the conversion of one into the other. Conversion between different forms of energy is not possible without losses.

Regarding heat, the same amount of heat can be of higher quality if it is available on higher temperatures. To investigate heat transfer ability Guo et al. (2007) introduced a new physical quantity: entransy. The conversion of higher temperature heat to lower temperature heat is easy, but in the reverse direction it is not possible without using additional work.

Exergy, however, makes a difference between higher and lower quality energy. In the calculation of exergy not only the first, but the second law of thermodynamics are also taken into account. By definition, exergy is the maximal possible useful work during a process that brings the system into thermodynamic equilibrium with a heat reservoir. This heat reservoir usually is the environment. Exergy of heat transfer can be expressed in the form of Eq. (2.1). It is clearly visible that the Carnot-efficiency shows the quality of heat.

$$E = \dot{Q} \times (1 - \frac{T_0}{T}) \tag{2.1}$$

Physical exergy of material streams is Eq. (2.2).

$$E = (\dot{H} - \dot{H}_0) - T_0 \times (\dot{S} - \dot{S}_0) \tag{2.2}$$

We can summarise the advantages of using exergy analysis: it can handle all types of energies together, it takes irreversibility into consideration and expresses that heat and work are not equivalent. Moreover, it also shows that heat degrades from higher temperatures to lower temperatures. A simple enthalpy balance fails to indicate these differences between different forms of energy. For this reason exergy analysis shall be in focus during design.

Exergy analysis can be applied in several forms. Researchers investigating exergy have discussed the development of new exergy analysis methods and models that quantify exergy loss and thermodynamic efficiency of distillation columns like Fonyó's two-part article of reversible distillation (Fonyó 1974a) and of finite cascade models (Fonyó 1974b). Bandyopadhyay (2007) based the exergy calculations on Invariant Rectifying and Stripping (IRS) curves. Zhu (2008) developed a method to allocate Cumulative Exergy Consumption between useful products.

In other cases the basic equations of thermodynamics related to exergy are used for calculations to obtain thermodynamic efficiency of distillation systems. Kencse and Mizsey (2009) use exergy analysis in parallel with greenhouse gas emission and later combined with both greenhouse gas emission and cost assessment (Kencse and Mizsey 2010). Suphanit et al. (2007) and Koeijer and Rivero (2003)also used this method, and recent publication by Sun et al. (2012) include the same principle for exergy analysis of distillation systems.

Exergy analysis can also be applied for the examination of complex distillation plants to locate process sections where exergy losses are high and improvements are possible. Rivero et al. (2004) used exergy analysis to detect critical point where improvements could be made.

The second law of thermodynamics postulates that entropy in a closed system can only increase. In the distillation process the heat is introduced into the system through the reboiler, then through the column where the useful work is done. Finally it is extracted from the system in the condenser at a lower temperature than it was introduced to the reboiler. This process makes it possible to separate the liquid mixture, and during this process heat degrades.

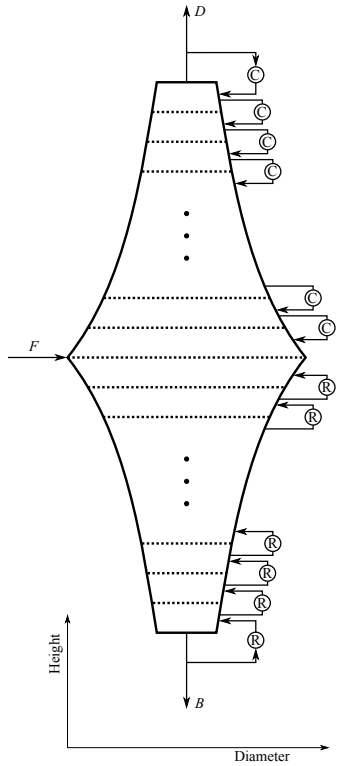


Figure 2.2: Reversible Distillation Column

The ideal distillation column, considering exergy, is the reversible distillation column (Figure 2.2) introduced by Fonyó (1974a). It is called reversible, because irreversible change does not occur in it; thus, there is no entropy generation. To achieve this, infinitesimal mass transfer gradient is needed in every point of the column, that also means an infinite number of plates, as well as negligible pressure drop. Heat transfer has to be distributed along the height of the column at each tray, and as a consequence, the number of heat transfers is also infinite, and the quantity of each heat transfer is infinitesimal. Below the feed only heat inputs and above the feed only heat outputs are applied. This implies that the material flow also changes along the height, resulting in an unusual column shape.

These very strict criteria of the reversible column render it a theoretical, infeasible solution. However, many of its features can be implemented during design of distillation columns. Thermally coupled distillation systems with side-stripper, side-rectifier, or heat integration are all solutions pointing towards this column, to improve energy efficiency; that is, efficient heat utilisation. Multiple feed inlets and multiple side-draws are also desirable. As well as these solutions internal heat transfer and even distribution of heat inputs and outputs are also required to build a thermodynamically efficient system. Moreover, ptimisation of feed stages and feed thermal state is also necessary. In certain cases heat pumps can also be applied. The more the distillation system resembles the ideal column, the more effective the distillation will be.

2.3 Economic Evaluation

As the purpose of building plants is the profit gained through production, in the very beginning, before choosing the appropriate system, a rough cost estimation is done for all systems. The capital cost is estimated with the appropriate equations proposed by Douglas (1988). This method uses different functions with different equipment types, and modifiers that depend on the material of equipment and circumstances of operation. Material prices are actualised with the usage of Marshall and Swift index. Costs consist of two types: annual operating cost is the cost of energy and utilities, while the other type comes from the investments needed to set up the plant. The total annual cost (TAC) is calculated as the sum of the annual operating cost and the annual capital cost (Eq. (2.3)). The annual capital cost is the capital cost of the plant or system distributed evenly during the designed plant lifetime (Eq. (2.4)).

$$TAC = Annual\ Capital\ Cost + Annual\ Operating\ Cost \tag{2.3}$$

$$Annual\ Capital\ Cost = \frac{Capital\ Cost}{Plant\ Lifetime} \tag{2.4}$$

This kind of cost estimation is quite simple, but at the beginning of the design it is satisfactory to estimate differences between alternatives.

2.4 Estimation of Greenhouse Gas Emission

Beyond thermodynamic efficiency and profitability there still is another important factor that shall be considered, and this is the impact on the environment. Distillation usually has no side-product or waste; therefore, there is only one emission to consider: the greenhouse gas emission. The enormous heat demand of the process needs a lot of energy that can only be satisfied in industrial volume by burning hydrocarbons. In the past few decades efforts have been made to regulate the emission of greenhouse gases. These gases have the potential to cause global warming and, thus, climate change when emitted to the atmosphere. Kyoto protocol put the emission of these gases on an economical base through emission quotas. It is possible to trade with quotas and this makes reduced GHG emission beneficial in both economic and environmental sense. CO_2 is emitted in the largest quantity, but other GHG gases also have effect on global warming. The calculation of effects is simplified with the calculation of CO_2 *equivalent* emission (CO_2e) with the help of the global warming potentials (GWP). Some example GWPs can be found in Table 2.2. Emissions of gases are multiplied by their GWP and summarized (Eq. (2.5)). However in the case of distillation, CO_2 has the major role, as burning fuels emits only small amounts of other GHGs.

$$CO_2e = \sum (GWP \times GHG\,emission) \tag{2.5}$$

Greenhouse gases	GWP value/100 years
Nitrous oxide (N_2O)	298
Methane (CH_4)	25
Trifluoromethane (HFC-23)	14800
1,1,1,2-Tetrafluoroethane (HFC-134a)	1430
Sulfur hexafluoride (SF_6)	22800

Table 2.2: GWP values and lifetimes from 2007 IPCC AR4 (Climate Change 2007)

In the complex methodology, during the comparison of different distillation structures the annual CO_2e emission is taken into account as an indicator of performance.

2.5 Process Control

Process design also involves the process control investigations, i.e., study of the controllability features of the structure, control structure design, etc.

In modern industrial plants the process control is essential. The process control equipment and technology usually costs more than the controlled equipment itself, which suggests enormous importance. Product quality, as well as corporate business plans rely on proper control of plants. Therefore, good controllability is needed to maintain optimal conditions in systems, otherwise the product quality or the profitability may deteriorate. Moreover, security is also ensured by properly working, stable control systems.

Distillation was one of the first industrial process that first applied process control, and it still is one of the most important direction of research. One distillation scheme may have many alternative control structures, even the controller structure has more alternatives. Multivariable (multi input — multi output, MIMO) and single variable (single input — single output, SISO, decentralised) controllers can be used. In the industry decentralised control systems are used for many reasons, e.g. they are simple, easy to use, and direct. It is called decentralised, because the Controlled Vatiables are controlled independently. In modern process control technology, usually a supervisory control sets the setpoints of the individual control loops. If a control loop is easy to operate, the supervisory control can control smoother. Skogestad (2004) also preferred decentralised controllers over multivariable controllers in his work about control structure design, because their simplicity yields in robustness and lower cost. When a certain scheme is chosen the next step is to design the control structure that maintains the desired product quality and ensures safe operation of the system.

Decentralised control is possible through modification of different properties (modified variables, MVs) while monitoring other properties (controlled variables, CVs) that shall be kept at certain values (setpoints, SPs). This is called the control loop. A the process of choosing the most adequate MV and CV pairs is called pairing. One MV can only paired to one CV. There are several independent properties of products that need to be controlled, and even more properties can be modified on a column. Thus, a large number of control loops are needed to be set up, and even larger number of pairings are possible. Variable pairing is an important step, wrong pairs can force the system into oscillation or out of control. To choose the most adequate solution among the possible pairings, rules-of-a-thumb can be found in literature, but in complex cases studies are recommended.

Morari (1983a) has shown that the best performance that any controller can achieve on a plant is a function of the plant itself. Investigation of the design alternatives from the view of controllability can predict their controllability features in advance, not knowing anything about the controller structure. Therefore, the first controllability considerations should begin at the conceptual stage of process design, where emphasis is placed on the screening of the flowsheet alternatives and such a control structure should be designed which shows good control performance and fulfils the process requirements.

2.5.1 Control Performance Indicators

One possible way of controllability analysis is the so-called closed loop simulation, where the system is investigated in time domain with an active controller. The performance of the system is measured by different types of integral errors. The other solution is the open loop simulation. That means: the control loops are not operating and the investigation is conducted in Frequency Domain. In this case the performance of the system is measured by Control Performance Indicators.

According to Skogestad, Lundström, et al. (1990) open loop simulations themselves are not interesting, but they can predict how sensitive the closed loop system can be to loads. The reason is, that if a system is not sensitive to loads without control, it is even more robust with a closed loop controller. Open loop investigations and indicators have been applied in the last decades but their usage is not universally accepted, they warn. Presentations of Luyben (1979, 1989) stated that regarding the large number of column configurations and their possible control structures, it is very probable that no universal tool exists which can simply differentiate between such configurations.

The controllability investigations in Frequency Domain are carried out in the early stage of process design and in this step the Control Performance Indicators are frequently used. There are several indicators that can qualify steady-state or dynamic behaviour. Birky et al. (1989) compared the methods of two column control experts, and found that those methods have only a few disciplines in common. The relative gain array (RGA) by Bristol (1966) and Shinskey (1979, 1984) is one of the mentioned indicators, but they also noted that a steady-state RGA cannot predict the dynamic behaviour. Skogestad, Jacobsen, et al. (1990) discussed the defects of the steady-state RGA through an example with DB control structure, i.e., distillate composition is controlled by distillate flow, and bottoms composition is controlled by bottoms flow. This control is overspcified regarding material balance; thus,it has bad steady-state RGA value.

In spite of this, they found such a control stable and satisfactory.. Gross et al. (1998) investigated a thermally coupled distillation structure. They compared three alternatives of control structure. Their work has covered steady state and dynamic investigations, in which they calculated singular values, condition numbers and RGA-based indicators in Frequency Domain. From their results it has been concluded that Frequency Domain indicators do not show unambiguous results for controllability, i.e. ranking of configurations is different according to different indicators.

Control Performance Indicators can also be calculated by Singular Value Decomposition (SVD). These indicators are Condition Number (CN) and Morari Resiliency Index (MRI).

Singular Value Decomposition can be seen in Eq. (2.6). G is an l × m matrix, is an l × 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 × l unitary matrix of output singular vectors, u_i, V is an m × m unitary matrix of input singular vectors v_i and H denotes the complex conjugate transpose of the corresponding matrix (Skogestad and Postlethwaite 1996).

CN of the transfer function matrix is the ratio between the highest and lowest singular values Eq. (2.7).

$$G = U \sum V^H \tag{2.6}$$

$$CN(G) = \frac{\overline{\sigma}(G)}{\underline{\sigma}(G)}. \tag{2.7}$$

where $\overline{\sigma}(G)$ is the highest singular value and $\underline{\sigma}(G)$ the lowest singular value of the transfer function matrix. CN lower than 10 indicates a well controllable process (Skogestad and Postlethwaite 1996). Theoretically, if the condition number is small the effects of the input uncertainty are always negligible, but large CN indicates model sensitivity in general. 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. However, this rule is not applicable in every case, therefore the control structure with large CN cannot be completely excluded from the applicable pairings without investigating other features.

MRI, the smallest singular value of the open loop transfer function, 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 variables (Morari 1983b).

Calculation of RGA can be seen in Eq. (2.8), where $\times$ is the Hadamard product and T denotes the transpose of the corresponding matrix.

$$RGA(G) = G \times (G)^{-T} \tag{2.8}$$

In the work of Bristol (1966) the RGA was 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 uncertainty (Haggblom 1997).

RGAno is defined in Eq. (2.9) and shows the deviation of the RGA from the unity matrix.

$$RGAno = \|RGA(G) - I\|_{sum} \tag{2.9}$$

2.6 Modeling Opportunities

For modelling purposes rigorous, nonlinear model of the distillation column is necessary. Different modelling concepts can be followed. Dynamic and steady-state simulations and indicators are used in different articles. Some authors used steady state indicators (Gross et al. 1998; Sågfors and Waller 1998; Segovia-Hernández et al. 2007; Zhang et al. 2011), other researchers preferred frequency dependent indicators (Alcántara-Ávila et al. 2008; Häggblom 1997; Horváth and Mizsey 2010; Murrieta-Duenas et al. 2011; Razzaghi and Shahraki 2007; Skogestad and Havre 1996; Vazquez-Castillo et al. 2009).

Controllers are used to keep the Controlled Variables at a constant value, i.e. the setpoint. However, the loads force the system into a dynamic behaviour; thus, dynamic simulations can yield more relevant information about the system. Bezzo et al. (2004) has showed the benefits of using process simulators especially for dynamic simulation: their work concludes that the best results can be achieved by dynamic simulations of the whole system with the control loops closed, i.e., all control devices are working. In this manner the behaviour of the system can be predicted with simple step disturbances in the compositions or flow rates, etc. In the course of such disturbances, the load rejection ability of

a control structure is investigated. However, such investigations require, plenty of time. The investigations' method follow the real-life test methods: the control loops have to be tuned properly, then the load rejection analysis is applied.

2.7 Aggregation of Different Indicators and Properties with Desirability Function

The purpose of investigating many factors in the same time needs an objective function. This objective function helps to evaluate alternatives according to various factors during design. An objetive function in industrial environment is simple if parameters can be expressed in the dimension of money. However, problems may arise when one tries to convert a certain parameter or indicator to money. Even the simplest indicators are useful for engineering, but their impact on profit or cost is not predictable, or only the direction of impact is sure.

The relationship between certain parameters and money is also related to regulations, that can change several times during the lifetime of the plant. As a general rule of thumb is that structures that have better performance in terms of engineering indicators, are less vulnerable to changes in regulations.

The aforementioned points of view encourage the use of engineering indicators and thermodynamic properties of systems as objective function instead of using money for this purpose. The next obstacle is to include more than one property or indicator in the objective function. For this purpose a handy tool can be used, the Desirability Function. The Desirability Function was proposed by Harrington (1965), and it is primarily used to convert multiple quality characteristic problems into single characteristic problems. First, each indicator is transformed into an individual desirability value d for the Desirability Function model. If the response is out of the acceptable range, the value of d becomes zero; if the response is at the target value, the desirability value d becomes one.

The individual Desirability Functions, d-s 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. (2.10)). This function makes the simple ranking of the process alternatives possible. This way there is only one number assigned to each case, and these numbers can be compared easily.

The $D - fct$ is defined as the geometric average of the k individual Desirability Functions. Desirability may include the designer priorities and desires by using the m weight factor, however, it is usually not applied. Instead, the

component functions d_k-s are constructed in a way to reflect the importance of each parameter. High value of $D - fct$ shows that all d_k are toward the target value that indicates the most adequate process alternative, and also includes the designer priorities and desires using the m weight factor (Derringer and Suich 1980).

$$D - fct = (\prod_{i=1}^{k} d_i^{m_j})^{\frac{1}{\sum m_j}} = (d_1^{m_1} \times d_2^{m_2} \times \cdots \times d_k^{m_j})^{\frac{1}{\sum m_j}} \tag{2.10}$$

In practice m_j weight factors are generally not considered, instead, d-functions are determined in a manner to reflect the importance of the given property. It is more straightforward and just as easy to express the importance in the conversion function instead of using weight factors in Eq. (2.10). Moreover, the form of the d-functions can have greater effect on the ranking than weight factors, therefore it is more important to use proper functions.

Desirability Function was successfully applied for complex engineering evaluation by Kencse and Mizsey (2010).

Chapter 3

Exergy Analysis

3.1 Introduction

Literature review shows that improving energy efficiency of distillation has been a continuous trend, and regarding the volume of distilled materials it still has a great potential. Reducing energy consumption is important both from economic and environmental points of view, as most of the energy consumption is still covered by fossil energy sources. Consuming energy also means emission of CO_2 and other flue gas compounds into the atmosphere. Many of these gases are considered to cause greenhouse effect and, at elevated concentrations, global warming.

Exergy Analysis is used in this thesis combined with the Total Site Integration concept. Two methods for application of Exergy Analysis are used in this work. One of them is the method presented by Kencse and Mizsey (2010) extended to 4 components instead of 3; consequently, to more complex distillation schemes. The drawbacks of this methodology are also shown as well as that simultaneous examinations of differnt boundaries can give a more adequate answer for questions of energy efficiency.

On the other hand a whole new methodology is presented, which shows that the Exergy Analysis can be used to improve performance of production sites. To handle operational problems, the new methodology includes some aspects of lean manufacturing principles. It enables designers of plants to handle the fact that operating conditions often differ from those that were specified for the design, and helps to make energy efficiency less prone to fluctuations in demand.

3.2 New Questions of Energy Efficiency

As the global economic environment challenges refineries in Europe, it has become vital to force changes in the processes. Several oil companies have started to adopt the lean manufacturing philosophy to give a new framework to the company's business. Some of these companies apply lean in certain fields, but for example the Hungarian Oil & Gas company, MOL Group has started full lean transformation of its whole business.

Lean manufacturing has its roots in automotive industry. It is based on and derived from the Toyota Production System, the management philosophy that had been developed through decades by Toyota after the Second World War. The idea has become famous after the book "The Machine That Changed the World: The Story of Lean Production" (Womack et al. 1991) was published in 1991.

Lean focuses on different aspects of production in order to ensure the flow of value. It is rather a set of techniques and philosophies than a very strict discipline. Despite the differences of the industries principles can be fitted on several processes.

According to the lean philosophy one of the main inhibitors of value flow is inflexibility. It is important to reduce inflexibility in order to shorten lead time, to lower stocks, to quickly react to changes in demand, and to achieve just-in-time production. This approach also implies Stop & Go operation of plants and devices.

Basically, refineries have not been built flexible neither in terms of stopping and restarting nor considering feedstock. Usually there is only a slight variance in feedstock and products. This fact shows a possible direction for future improvements; thus, it is important to concentrate on the design of plants that have better energy efficiency, while they are more flexible than existing ones.

Apart from technological improvement the other way is to improve the mode of operation. Despite every efforts to develop more efficient distillation technologies economic environment can have bigger effect on the overall efficiency of a plant. Most of the design calculations assume that conditions are those of that the scheme was designed for. In reality plants are built for decades, during which period demand for the products fluctuate. Under the designed load efficiency of plants usually decline, and in some cases Stop & Go operation of the plant can be more efficient. However, stopping a plant has effects on connected plants, heat integrations may be separated. This changes the behaviour and the efficiency of the running plant. This effect has to be examined.

Heat integration, or more broadly: energy integration is also feasible between different processes like feed preheat, not necessary within distillation. The two different approaches whether to solve heat integration in the same process or to integrate different processes might be equally efficient in certain cases, but their flexibility can be different.

Energy efficiency is very important to maintain competitivity; however, changing conditions and demands can have a huge negative effect on specific, and overall efficiencies. If a plant is not operating at full capacity, the specific energy consumption deteriorates. Due to the large quantities of separated materials, the energy consumption of distillation in the world is very high. As large amount of energy is used in refineries and petrochemical plants, every small improvement yields in great savings. It is not unusual that modifications of processes have a rate of return measured in a few months.

Flexibility, however, challenges present technologies and equipment. It has to be implemented early, in the design phase, and it makes the design more

complex due to the large number of possibilities in operating modes. Several operating modes are already applied in continuous plants and the number of modes shall be increased for a truly flexible industrial site. The more plants the site has, the more possible combinations of operating and stopped plants are possible. Moreover, these plants can have many modes for producing different product qualities resulting in even higher number of possibilities.

In such a flexible scenario it is possible that two plants are running heat integrated to each other, but one of the units have to be stopped. In this case the efficiency of the whole site may decrease. Depending on the structure of the systems this drop can be smaller or larger depending on flexibility. This is something that has to be evaluated in order to be able to choose which solution to use.

3.3 Dual Exergy Analysis and Flexibility

Considering flexibility, it is important to separate the core process, that has the same parameters in all conditions where the given process may work. The core process is of which the properties do not change regardless of the state of integration. The parameters of the core process have to be constant to ensure the desired separation. *The exergy loss in the core process is necessary to achieve the desired separation with the chosen system. All other exergy losses depend on the technological environment.* As two extreme cases this core process can be integrated to an Ideal Background Heat Cascade or used independently, applying universal cooling and heating utilities. These cases are the most and least ideal cases of a flexible industrial site that a process can face. In the first scenario, all energy leaving the process is utilised in full, as the ideal background heat cascade needs heat at exactly the same temperatures as the core process can provide, and it also provides heat at the desiredt level. In the latter case the heat is provided at higher level than needed and carried away by cooling water at lower temperature than the condenser provides, without using any portion of it. Such case can happen when the processes that provide the background heat cascade are stopped, and the heating and cooling tasks are accomplished with universal utilities. In the aforementioned cases the energy efficiency of the core process remains the same but the overall process energy efficiency decreases with universal utilities, as a great exergy loss occurs outside the boundaries of the core process. Universal utilities are those that can be used in most applications, like steam networks or cooling water taken from the environment.

In practice the difference between the cases means different boundaries for

the analysis that are the boundaries of the processes, i.e. the heat cascade or the environment.

In this sense the real importance of boundary is the presumption that all exergy leaving the system is utilised outside the system as is. This means that heat is fully utilised elsewhere in the Ideal Background Heat Cascade at the temperature at which it crosses the boundary. In other words: the exergy of the stream, that is crossing the boundary, is useful; no portion of it is lost due to temperature differences until it reaches the next process in line where it is utilised at the same temperature. Otherwise the boundary does not represent the system well, and needs to be redefined.

Core Process (Case #1)

In the forst case when the system boundary is right around the core process. It means that the heat exchanging temperatures are exactly those of the materials involved in the core process, liquids and vapours of the distillation (see Figure 3.1, dashed) entering the heat exchanger. This approach presumes infinite possibilities of applicable utilities. In this case even the usual temperature differences needed for heat transfer are not taken into account, and this case then most strictly describes the distillation process, the separation of materials without auxiliary unit operations. This case is analogue to the ideal case of a distillation system integrated into a large site with infinite possibilities in integration, and infinite possibilities of temperature levels of heat exchange.

This is the case that investigates the core process. The Exergy Analysis is carried out under the assumptions that:

- the driving force of heat transfer is zero for the sake of simplicity($\Delta T = 0$),
- there is a background process/heat cascade, that can deliver and accept (source-sink) heat at every temperature level (total site problem),
- the heating in the reboilers and the cooling in the condensers takes place with streams obtained from the background process at zero driving force,
- there is no anergy (destroyed exergy) during the operation where the products of rectification cools down to the ambient temperature, since their exergy is fully utilised in the background process also at zero driving force.

The distillation process is totally and optimally integrated to an Ideal Background Heat Cascade; thus, it has the maximal efficiency possible for the given

scheme. Efficiency of an operating plant as part of any site can only be lower than this. With this boundary only the exergy loss of distillation is calculated.

In a less theoretic case a problem with this approach arises. The exergy that is leaving the system is regarded useful; however, placing the boundary one step further we encounter the next temperature decrease without associated useful work. In heat exchangers heat exchange surface is finite; thus, there must be a temperature difference. Moreover, a certain temperature difference is defined in order to optimise costs. This means, that the heat crosses the boundary at a lower temperature, than in the case of the core process. In these cases some exergy is lost: higher temperature heat enters the system, than the process really needs; and lower temperature heat exits, than the process provides. Furthermore, this is still an idealistic approach. It still assumes that heat leaving the system is used in another process exactly at its temperature of leaving the heat exchanger. If the temperature of utilisation in the next unit is lower than the exit temperature of the stream from the preceding unit, the difference in exergy is lost.

Standalone Mode (Case #2)

Considering the loosest boundaries (Figure 3.1, dotted dash) the stream crossing the boundary has 0 physical exergy, as no other process uses the extracted heat. This happens in the case of a single processes or when the temperature is so low, that its heat content cannot be utilised any more, and it is released into the environment with cooling water or in other forms. In this case the heat provided by the process is not used at all.

Regarding a single distillation plant as the whole site, the exergy loss in the core distillation system is the same as in the integrated case, but the whole process with all auxiliary processes and streams have a greater exergy loss. Without further integration, the exergy content of all exiting streams are wasted.

This case is fully based on a single distillation system without a background process. That means, that there is only one unified heat source: a steam system; and there is only one unified heat sink: the cooling water taken from, and sent back to the environment at ambient temperature. Steam systems guarantee heat transfer between distinct plants far from each other. Some steam recovery may be possible, but it is not usual. In these rare cases the recovered steam is fed into a system with lower pressure than the original heat source. In other cases either higher pressure steam or shaft work may be used to regenerate it.

The heat that leaves distillation may be used in the plant or close to the plant, but in several cases it is taken away by the cooling water, or the hot

product may cool down during storage or transportation. Whichever way, the final state of the products will be the equilibrium with the environment, releasing heat without doing any work. Ultimately, all of the exiting exergy will become lost, as at the cold side boundary of the system the temperatures will be equal to the ambient temperature. This boundary is used in the Complex Methodology by Kencse and Mizsey 2010.

The Exergy Analysis in this case is carried out under the assumptions that:

- uniform cooling water is applied in the condensers, and product cooling operations to ambient temperature (final bottom product too).
- the driving force of heat transfer is zero again. Utilised cooling water is not used anywhere else, and its exergy content is calculated as anergy (exergy loss),
- uniform heating medium is applied in the reboilers.

Flexible Production Site

In a felxible site, the integration possibilities vary between these two extremities. When several plants are operating at the same time, it provides a large heat cascade, but when all other plants are stopped, the integration will become impossible. Therefore I investigate these two cases of boundaries.

In the first case, the boundaries are around the core process of distillation. In the second case, the individual site is considered, with no further integration possibilities. The models are simplified as much as possible: there is no temperature difference needed for heat transfer, meaning zero driving force in all cases.

3.4 Calculation Basics

The used method to calculate the exergy loss and thermodynamic efficiency is described by Seader and Henley (2006). First the irreversible entropy loss (Eq. (3.1)) needs to be calculated.

$$\Delta \dot{S}_{irr} = \sum_{out} (\dot{n} \times s + \frac{\dot{Q}_C}{T_C}) - \sum_{in} (\dot{n} \times s + \frac{\dot{Q}_R}{T_R}) \tag{3.1}$$

Having the entropy loss calculated and knowing the temperature of the heat reservoir, it is possible to calculate the exergy loss (Eq. (3.2)).

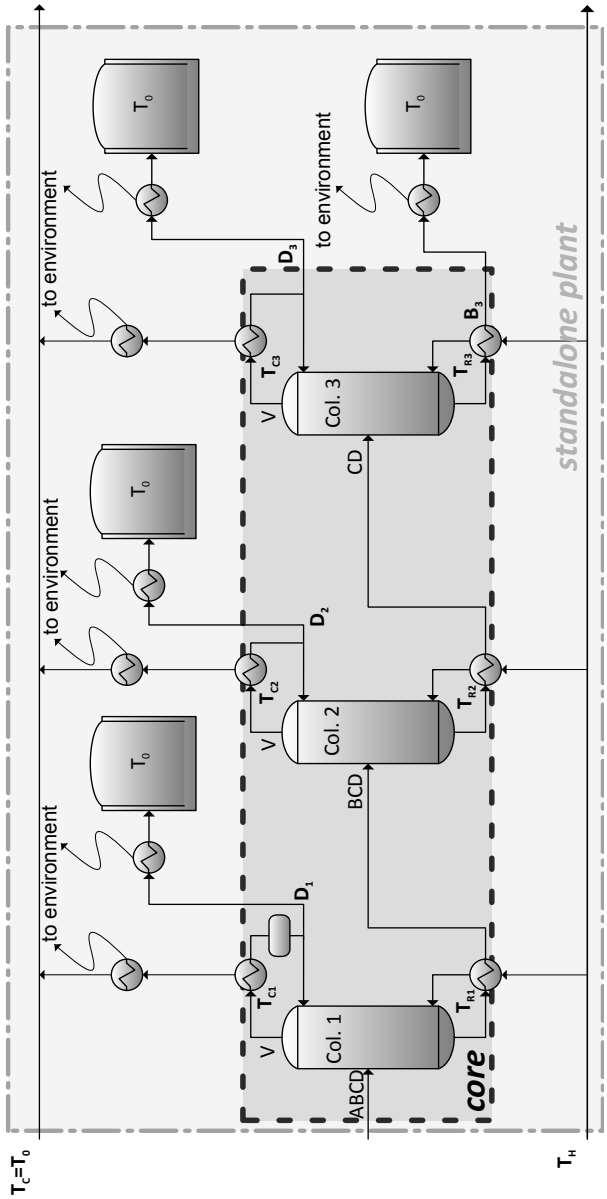


Figure 3.1: Boundaries of Exergy Analysis

$$\dot{E}_{loss} = T_0 \times \Delta \dot{S}_{irr} \tag{3.2}$$

Exergy loss (lost work/anergy) can also be calculated directly from the availability (exergy) balance (Eq. (3.3)).

$$\dot{W}_{loss} = \sum_{in} \left[\dot{n} \times e + \dot{Q} \left(1 - \frac{T_0}{T_R} \right) \right] - \sum_{out} \left[\dot{n} \times e + \dot{Q} \left(1 - \frac{T_0}{T_C} \right) \right] \tag{3.3}$$

The work of separation is also needed; that is, the difference of the exergy flowing in and flowing out with material streams (Eq. (3.4)).

$$\dot{W}_{sep} = \sum_{out} (\dot{n} \times e) - \sum_{in} (\dot{n} \times e) \tag{3.4}$$

Finally, the efficiency is calculated by dividing the minimal useful work by the overall energy input.

$$\eta = \frac{\dot{W}_{sep}}{\dot{W}_{sep} + \dot{W}_{loss}} \tag{3.5}$$

3.5 Four Component Case Studies

In the following, case studies are presented on two different quaternary mixtures. The two cases of boundaries for Exergy Analysis represent a plant with different conditions, being part of a flexible production site.

Different distillation schemes, that complete the same separation task, are compared according to the following parameters:

- Thermodynamic Efficiency
- GHG emission
- Total Annual Cost of Investment and Utility

Apart from the design parameters the aforementioned circumstances of exergy analysis are also investigated. In the exergy analysis the ambient temperature is 10 ℃, as it is the yearly average temperature in Hungary (OMSZ 2013). However, in Section 3.8 a test is carried out on the influence of ambient temperature on the results of Exergy Analysis.

In the cost estimation, designed lifetime of the systems is 10 years with 8000 annual operating hours. Due to the importance of distillation in hydrocarbon processing industry the two quaternary mixtures are the following:

- alkane hydrocarbons,
- aromatic hydrocarbons.

Alkane hydrocarbon mixture is an equimolar mixture of

- n-pentane (boiling point: 36.1 ℃)
- n-hexane (boiling point: 68.5 ℃)
- n-heptane (boiling point: 98.4 ℃)
- n-octane (boiling point: 125.5 ℃).

While the aromatic mixture is also an equimolar mixture of

- benzene (boiling point: 80.1 ℃)
- toluene (boiling point: 110.6 ℃)
- ethylbenzene (boiling point: 136.0 ℃)
- cumene ((1-methylethyl)benzene, boiling point: 152.0 ℃).

Additionally two cases of product purity were examined with both mixtures:

- sloppy separation with lower purities (ALK-LP, ARO-LP),
- sharp separation with relatively high purities(ALK-HP, ARO-HP).

Alkane product purities can be seen in Table 3.1, and aromatic product purities are listed in Table 3.2. Product compositions were determined by the least tunable structure.

The base case is the conventional direct sequence (DS, Figure 3.2). Additionally, a backwards heat integrated alternative of the direct sequence is also among the alternative structures (DS-BHI, Figure 3.3). Forward integration proved to be uneconomic according to a previous study by Emtir et al. (1999), therefore, it is not investigated in this study.

A modified version of the direct sequence is also examined (DS-EP, Figure 3.2): the pressures in Col. 2 and Col. 3 are equivalent to those of the backwards heat integrated scheme (DS-BHI). This system helps to make a distinction

Table 3.1: Compositions of *alkane* hydrocarbon product streams (mole fraction)

		Distillate 1	Distillate 2	Distillate 3	Bottoms 3
Sloppy	n-pentane	**0.82**	0.18	0.00	0.00
	n-hexane	0.15	**0.70**	0.15	0.00
	n-heptane	0.03	0.12	**0.63**	0.23
	n-octane	0.00	0.00	0.22	**0.77**
Sharp	n-pentane	**0.96**	0.04	0.00	0.00
	n-hexane	0.04	**0.93**	0.04	0.00
	n-heptane	0.00	0.03	**0.90**	0.06
	n-octane	0.00	0.00	0.06	**0.94**

between the effects of integration, and the effects of modifications needed for integration. Backwards heat integration needs elevated pressures compared to the first column to be able to achieve temperatures high enough to realise the necessary heat transfer between the source and sink columns.

Apart from the direct sequence structures, columns with side products are also examined. One of them is a single column with four products (SC, Figure 3.4), the other one is the same single column but with a furnace producing vapour feed (SC-OHV, Figure 3.5). These structures are also integrated in a sense: they are several columnson top of each other, like columns are "vertically" heat integrated distillation steps. A disadvantage of single columns is that product purities are not as flexible and independent as in the case of other structures, at least without side strippers or side rectifiers. For the sake of simplicity, these equipment were omitted from simulations, and the other structures were set up to achieve same separational performance as the single columns could provide.

In order to have the same product streams and work of separation all the product streams have the same pressure at the boundary. In the case of DS-EP and DS-BHI some of the products leaving the columns have higher pressure than in the base case, where all columns operate on atmospheric pressure. In these cases an additional heat exchanger is included, in order to reduce pressure to atmospheric, while keeping the mixture in liquid phase. In this case, the heat duties of product heat exchangers are considered.

For simulations the Aspen Plus software is used. The chosen thermodynamic property is Peng-Robinson, as in the very beginning of the work anomalies have been experienced with Soave-Redlich-Kwong (SRK) property model.

Table 3.2: Compositions of *aromatic* hydrocarbon product streams (mole fraction)

		Distillate 1	Distillate 2	Distillate 3	Bottoms 3
Sloppy	benzene	**0.78**	0.22	0.00	0.00
	toluene	0.15	**0.75**	0.10	0.00
	ethylbenzene	0.05	0.03	**0.63**	0.29
	cumene	0.02	0.00	0.27	**0.71**
Sharp	benzene	**0.98**	0.00	0.00	0.00
	toluene	0.02	**0.98**	0.00	0.00
	ethylbenzene	0.00	0.00	**0.93**	0.07
	cumene	0.00	0.00	0.07	**0.93**

Further parameters of distillation columns can be seen in Appendix A.

3.6 Results

3.6.1 Complex Methodology

The base of the methodology of Kencse and Mizsey (2010) is that energetic, economic and environmental Performance Indicators are considered together to choose the best separation system for a given separation task.

The focus of the exergy analysis is on the aforementioned distillation systems. All of them are considered standalone systems which means a chosen temperature for the heating and cooling utility to ensure equal conditions[1].

Figure 3.6 shows the thermodynamic efficiencies, the results of Exergy Analysis. Comparing these ranks with the results of GHG emission analysis, cost estimation, and total enthalpy input of systems (Figures 3.7, 3.8, and 3.9) it is obvious that all of the systems have quite similar tendencies in different Performance Indicators. Not the same rank in all case, but the differences are only minor, and often these differences are due to simulation software limitations. Consequently, with the given conditions all these indicators in these cases

[1]Schemes with overheated vapour have higher temperatures in the furnace (in some cases not even realistic temperatures, good only for comparison) and *these* temperatures are considered in calculations instead of the unified steam temperature because using it would make unwanted advantage in the results.

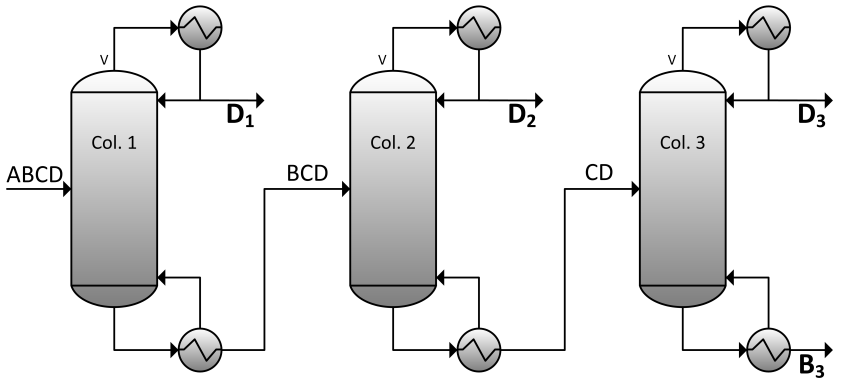


Figure 3.2: Conventional Direct Sequence (DS, DS-EP)

are strongly correlated, and do not reveal much useful information if they are calculated together.

The same rank by total annual costs and enthalpy shows that in these cases the heating was responsible for most of the costs. At the same time CO_2e emission is only caused by hydrocarbon burning that ensures heating of systems.

As the utilised heat is from the same source in all cases, the difference in exergy loss only comes from the difference of quantities of the utilised heat. In other words, exergy balance is simplified practically to an enthalpy balance with limited number of heat transfer temperatures. Further aggregation of exergy and other performance indicators that rely on enthalpy would not be beneficial in several cases.

3.6.2 Exergy Analysis in the Case of the Core Distillation Process (Case #1)

In this case, only the exergy loss of distillation is important,the distillation system is totally and optimally integrated to an Ideal Background Heat Cascade.

If we take a look at the results, Figure 3.10 shows an unusual tendency in the case of direct sequence structures. The most simple direct sequence (DS) prove to be the most efficient in all cases. Moreover, the heat integrated direct sequence is worse in both cases than its sibling structure without heat integration (DS-EP).

These results may be surprising at first sight, but after taking a second look

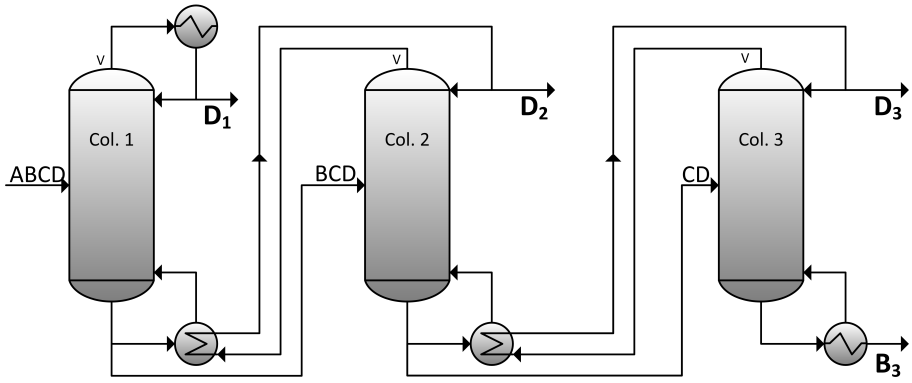


Figure 3.3: Direct Sequence with Backwards Heat Integration (DS-BHI)

at it all these phenomena can be explained. The first thing to mention is the higher efficiency of lower pressure systems. At higher pressures vapourisation of liquids requires molecules with higher energy and, thus, the boiling point rises. In terms of exergy higher temperature heat is of higher quality; therefore, a more valuable energy is used for the same separational work, which means that efficiency is lower at higher pressures.

The second thing to consider is the difference between the DS-EP and DS-BHI schemes. What one would expect is that the heat integrated structure has at least the exergetic efficiency of the non-integrated scheme. Technically they are the same in these cases, however, exergy analysis makes a difference. During the design of the DS-BHI, the pressures were set to levels that ensure proper temperature difference between the two sides of the common heat exchangers of neighbouring columns. This temperature difference is chosen as a rule of a thumb, and its aim is to ensure finite area surfaces. Due to the assumption that outside the system no driving force is needed, the designed temperature difference is disadvantageous in this case of boundaries. DS-EP structure operates on the same temperatures and on same pressures as DS-BHI, and produces the same products, has the very same inner flows. But, in the case of DS-EP, heat is not transferred between the columns, instead it is exchanged with the ideal background heat cascade, where the heat makes useful work while it is cooled down to the temperature, at which it enters the investigated distillation system again.

The better efficiency is achieved because the exergy difference, originating

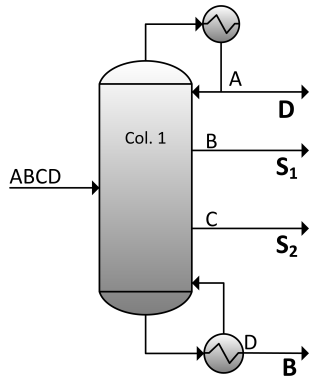


Figure 3.4: Single Column with Side Products (SC)

from the temperature difference, is "spared". In other words, the heat distribution is more even in DS-EP structure. In the case of DS-BHI the heat input is at the highest temperature, and the heat output is at the lowest temperature while the DS-EP has heat transfer on six different temperatures. As it could be seen in the case of the reversible column, the distribution of heat transfers is a key for less exergy loss.

The most interesting result is the difference between the results of DS and DS-BHI configurations. Heat integration is a popular way to achieve lower energy consumption. In spite of the fact that heat consumption can be significantly reduced, these results show that despite sparing a lot of heat, this kind of heat integration is not necessarily the best solution. The reasons for the worse performance of the heat integrated scheme have been mentioned before: firstly, this kind of integration needs elevated pressures, which requires more exergy; secondly, heat transfer is better distributed without heat integration. On the one hand, DS scheme uses more energy; on the other hand it also provides more energy for other processes, and these energies are of higher quality when they pass the boundary.

One more thing deserves our attention: SC scheme has even better efficiency than DS-BHI in sloppy cases, when reflux rate is low. This shows that this kind of integration may be better, because it does not need any pressure elevation. The difference between SC and SC-OHV is easy to explain: the overheated vapour is heated to much higher temperatures, which is unnecessary. Moreover this solution wastes so much exergy, that it has the lowest efficiency of all.

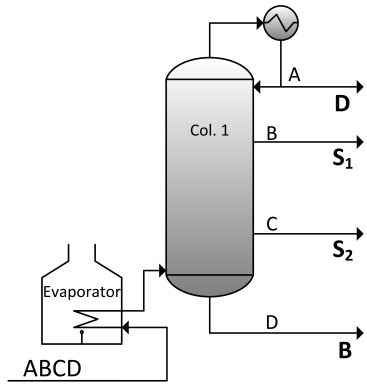


Figure 3.5: Single Column with Side Products and Overheated Vapour Feed (SC-OHV)

3.6.3 Exergy Analysis of Standalone Mode (Case #2)

This is the scenario when the investigated system has no integration possibilities. Uniform heat exchange temperatures are used, that usually are steam supply systems or unified cooling utilities, preferably cooling water (at ambient temperature). In this case, this situation is considered. Thus, all cooling temperatures are T_0, there is no further integration possibility. This means: all cooling temperatures are fixed at lower temperature than needed, and heating temperatures are higher than necessary.

This situation is quite realistic for even a medium sized plant that has no integration possibilities with other processes, or other processes are stopped. In this case, however, Exergy Analysis loses most of its meaning as differences in temperatures disappear. As the utilised heat is from the same source in all cases, the difference in exergy loss only comes from the difference in quantities of the utilised heat. In other words, Exergy Analysis does not provide more useful information than an Enthalpy Analysis.

Comparing efficiencies (Figure 3.11) with enthalpy consumption (Figure 3.7) shows that the ranks are the same. The similarities are obvious. In all cases the DS-BHI scheme has the highest efficiency and the lowest energy consumption.

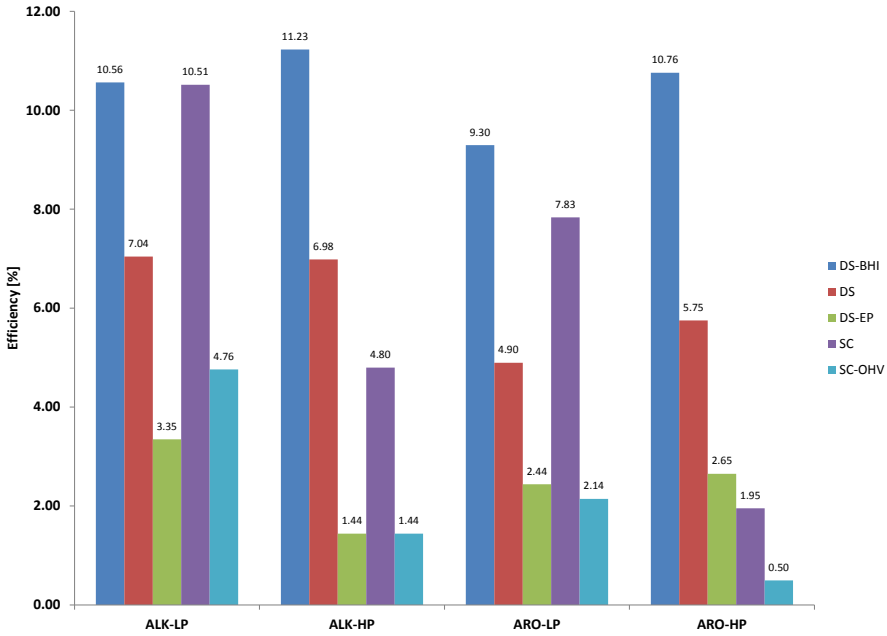


Figure 3.6: Efficiency

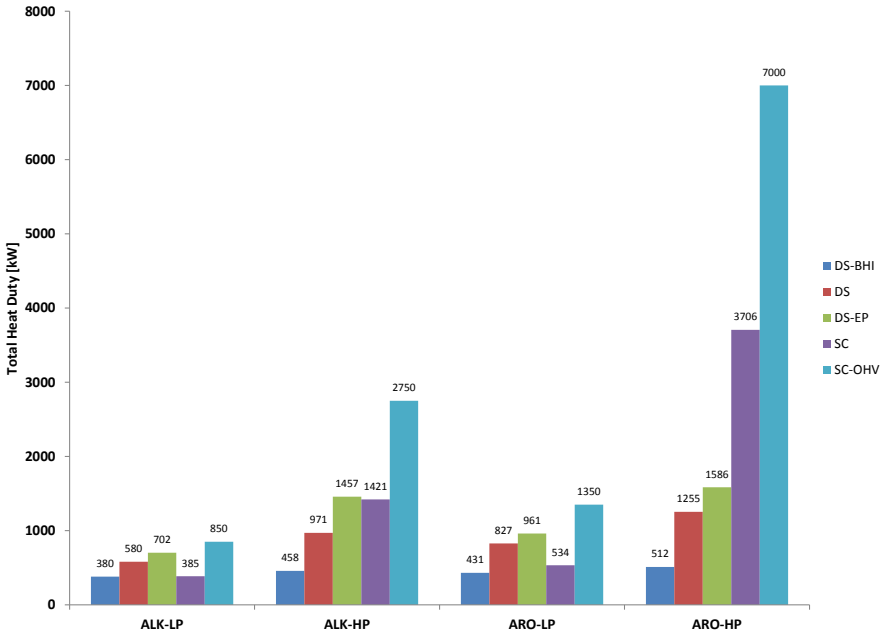


Figure 3.7: Total Heat Duties

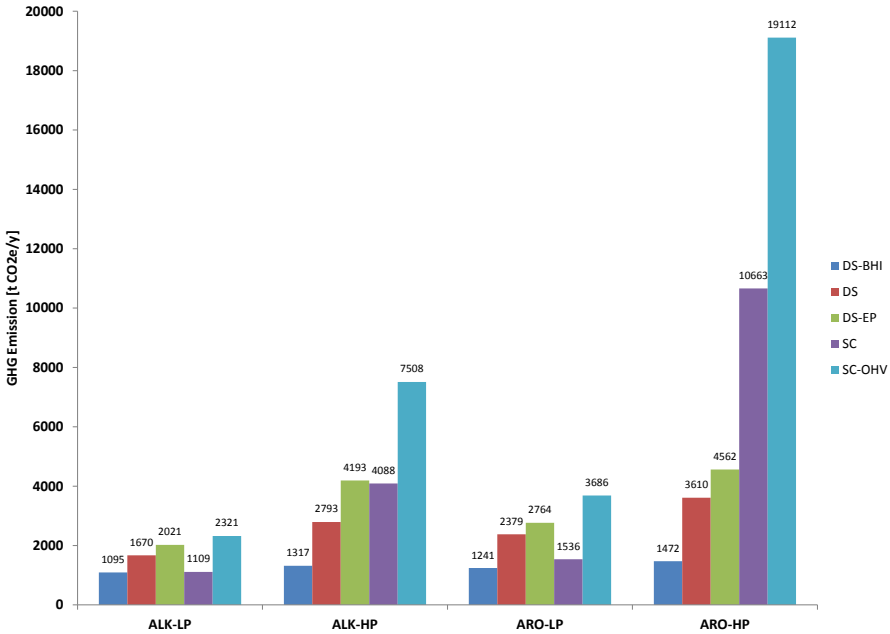


Figure 3.8: Greenhouse Gas Emissions

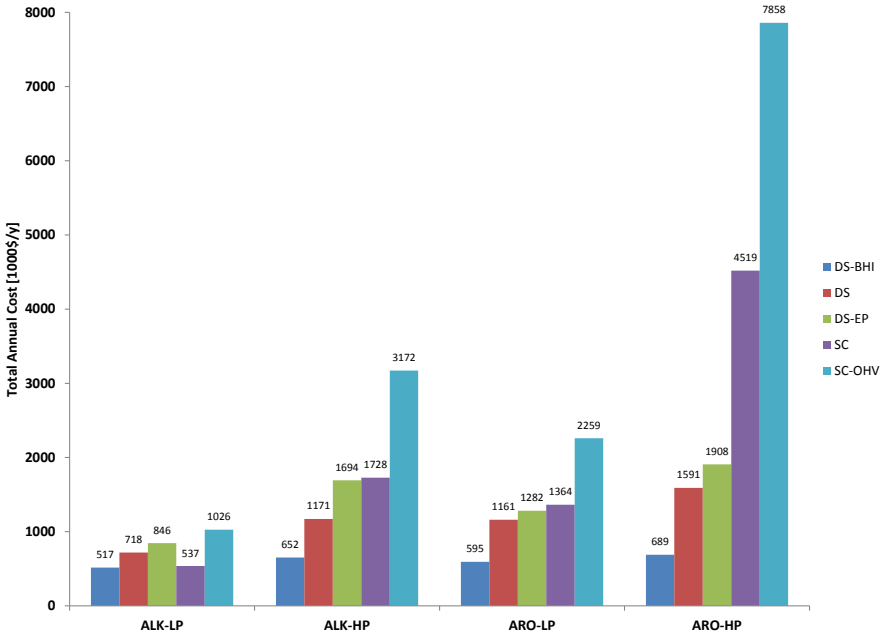
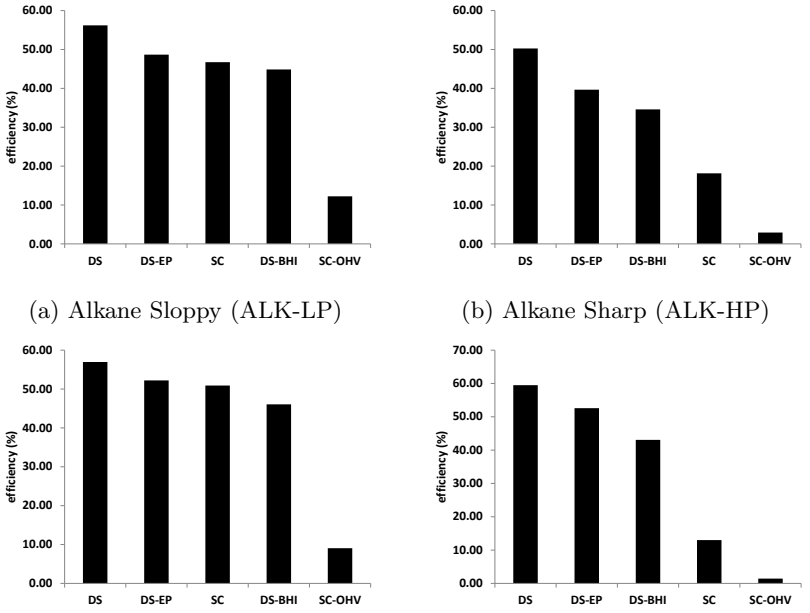


Figure 3.9: Total Annual Costs (1000 $\$/y$)



(a) Alkane Sloppy (ALK-LP)

(b) Alkane Sharp (ALK-HP)

(c) Aromatic Sloppy (ARO-LP)

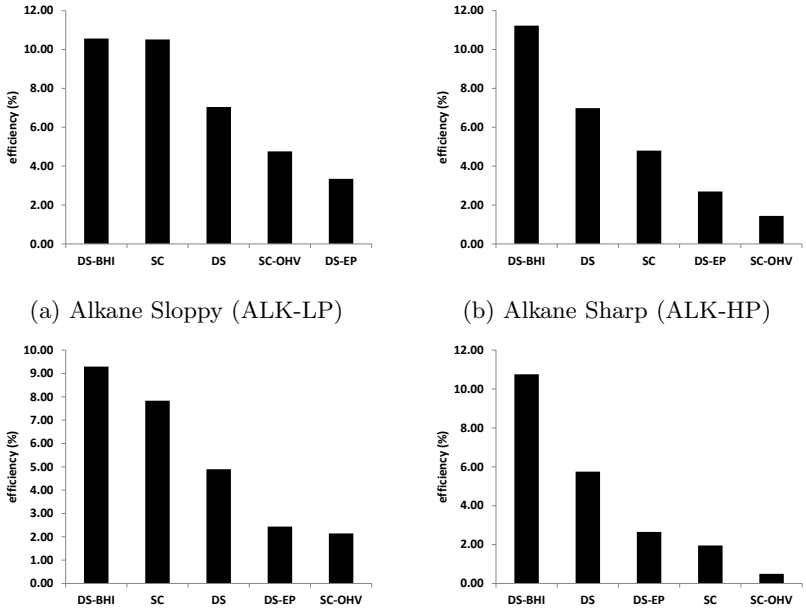
(d) Aromatic Sharp (ARO-HP)

Figure 3.10: Thermodynamic Efficiencies of the Core Distillation System

3.7 Comparison of Operating Modes

As the results show, the very same distillation schemes can be evaluated as efficient and less efficient, depending on the integration level with the surrounding site that means different system boundaries. As a part of a flexible site, the possibilities can vary between the ideal heat cascade integrated mode and standalone mode. Theoretically the integration level can vary from day to day by changing operation modes of connected plants according to rolling plans. By moving the boundaries of the investigated system it is possible to test several conditions and to choose a system that performs well as part of a flexible site.

Case #1 shows that the heat integration in the same distillation process lowers exergetic efficiency compared to the distributed heat exchange of the simple direct scheme integrated to the ideal heat cascade. The ambivalent behaviour of heat integration can be explained in other words: a DS scheme consumes more



(a) Alkane Sloppy (ALK-LP)

(b) Alkane Sharp (ALK-HP)

(c) Aromatic Sloppy (ARO-LP)

(d) Aromatic Sharp (ARO-HP)

Figure 3.11: Thermodynamic Efficiencies in Standalone Mode

heat than DS-BHI, but at the same time it also provides more heat at the cold ends. And what is more important: majority of this heat is higher quality heat, at higher temperatures than those exiting heat integrated systems at the last column.

However, from flexibility point of view, heat integrated distillation scheme provides a steadier performance. In standalone mode, that is, if there was no Ideal Background Heat Cascade, just the distillation system itself, heat integration saves exergy compared to the Direct Sequence scheme by using less enthalpy, while the more provided enthalpy of the direct scheme cannot be used.

The previous cases are simple cases, however it already means sveral different cases, that would mean the same number of Composite Curves and Grand Composite Curves for a Pinch Analysis. Generally sites are lot more complicated. With Exergy Analysis it is simpler to test this large number of conditions and cases compared to Composite Curves; moreover, it can easily combine different

energy types.

It could be seen that heat integration within the same process is not necessarily a good solution as it may require modifications that lower thermodynamic efficiency. On the other hand, in a constantly changing environment its performance is steadier. It the ratio of time spent in standalone mode exceeds a certain limit, integration within distillation becomes more efficient then integration outside of the process.

The optimal processes highly depend on the whole site, whether it is used often as a standalone system with fixed and constant utility temperatures, or there is a site that provides possibility for integration.

Apart from site flexibility questions, the comparison of the current state and the core processes provides an opportunity to discover the exergy reserves in the examined process. This reserve reveals the potential that can be targeted with better integration with the site.

3.8 Sensitivity Test

Apart from the previously mentioned problems of choosing appropriate temperatures there may be another problem in connection with temperatures and Exergy Analysis. This is the selection of the ambient temperature. Ambient temperature on industrial sites changes even during a single day, and is dependent on many other factors also. These factors may be the the time of the year, weather, etc. Of course, there is a possibility of choosing average temperatures, but there is a chance that great variance of ambient temperature might corrupt the stability of ranking.

To check the stability, the efficiencies are also calculated at other temperatures. These temperatures are -10 ℃ and 30 ℃. The range between these temperatures is large enough to represent temperatures changes in most part of the world.

Basically the ranks should not change much, because altering the ambient temperature affects both the input and output sides of equations.

Table 3.3 shows that in Case #1, the ambient temperature does not affect the rank at all. However, Table 3.4 shows that in other cases the rank is not the same at every ambient temperature. In these cases altering the ambient temperature also induces some changes in the separation process, the storage temperature and the temperature of the cooling utility differ (change in ΔT).

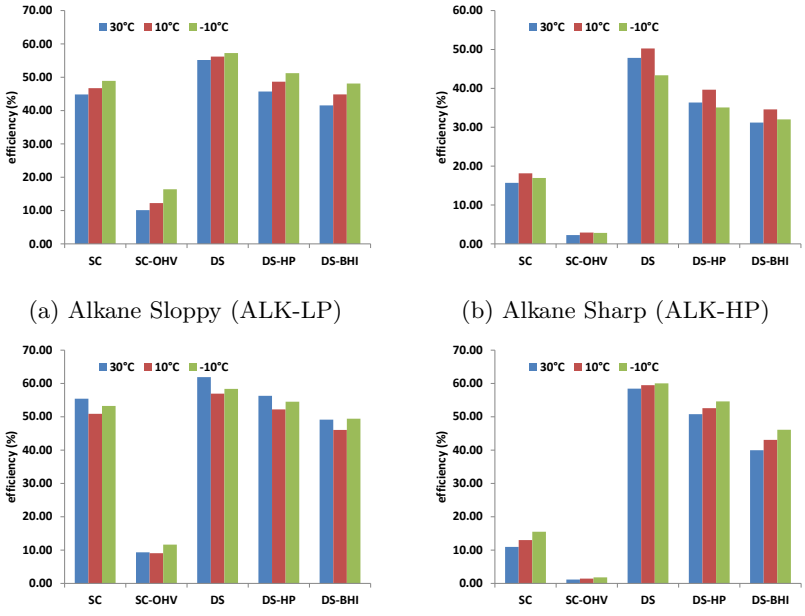
These differences, however, are just minor differences in efficiency. In every case when the rank changes, only two schemes change places, but the whole

Table 3.3: Ranks in Case #1

		SC	SC-OHV	DS	DS-EP	DS-BHI
ALK-LP	30 ℃	3	5	1	2	4
	10 ℃	3	5	1	2	4
	-10 ℃	3	5	1	2	4
ALK-HP	30 ℃	4	5	1	2	3
	10 ℃	4	5	1	2	3
	-10 ℃	4	5	1	2	3
ARO-LP	30 ℃	3	5	1	2	4
	10 ℃	3	5	1	2	4
	-10 ℃	3	5	1	2	4
ARO-HP	30 ℃	4	5	1	2	3
	10 ℃	4	5	1	2	3
	-10 ℃	4	5	1	2	3

Table 3.4: Ranks in Case #2

		SC	SC-OHV	DS	DS-EP	DS-BHI
ALK-LP	30 ℃	2	4	3	5	1
	10 ℃	2	4	3	5	1
	-10 ℃	1	4	3	5	2
ALK-HP	30 ℃	3	5	2	4	1
	10 ℃	3	5	2	4	1
	-10 ℃	3	5	2	4	1
ARO-LP	30 ℃	2	5	3	4	1
	10 ℃	2	5	3	4	1
	-10 ℃	2	4	3	5	1
ARO-HP	30 ℃	4	5	2	3	2
	10 ℃	4	5	2	3	2
	-10 ℃	4	5	2	3	2



(a) Alkane Sloppy (ALK-LP)

(b) Alkane Sharp (ALK-HP)

(c) Aromatic Sloppy (ARO-LP)

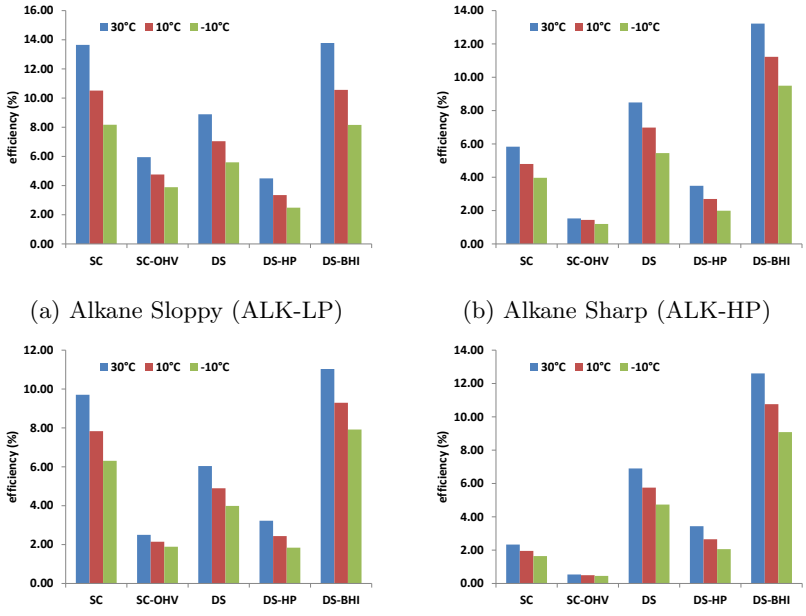
(d) Aromatic Sharp (ARO-HP)

Figure 3.12: Thermodynamic Efficiencies of the Core Dsitillation Process

rank is not rearranged at different temperatures. Moreover, in these cases, the differences between the rearranged schemes are minimal, or negligible (see Figure 3.12 and Figure 3.13). Which means, that from an exergetic point of view these schemes are almost equivalent, and other factors may decide during design, these disturbances affect results only in a very moderate way, and basically the ambient temperature does not induce large error in the exergy analysis.

3.9 Conclusion

Hydrocarbon industry and many other industries have already started to adopt lean thinking. It became obvious that mind-set has to be changed, processes have to be more flexible and inventories have to be reduced due to negative effects of fluctuations in demand and prices.



(a) Alkane Sloppy (ALK-LP)

(b) Alkane Sharp (ALK-HP)

(c) Aromatic Sloppy (ARO-LP)

(d) Aromatic Sharp (ARO-HP)

Figure 3.13: Thermodynamic Efficiencies in Standalone Mode

Plants that were designed several years and often decades ago experience problems while following fluctuating rolling plans. Underutilisation has greater negative effects on plants specific energy consumptions than any technological improvement can counterweight; thus, Stop & Go operation or more flexible technologies would be desirable if it is possible to solve.

After other fields lean principles can also appear in design, and industrial sites can be less prone to economic instability in terms of energy efficiency.

From lean manufacturing point of view flexibility of processes is important, and by using Exergy Analysis energy efficiency can be easily evaluated to find the optimal alternative from the set of possible solutions. This solution is as flexible as needed and is energy efficient at the same time. The proposed new method of using Exergy Analysis grants access to new information that was neglected before, morover with it it is possible to handle evaluation partly automatically.

Exergy Analysis combined with simulations of plants and different scenarios

of average downtimes can yield in a site that has good and steady specific energy consumption regardless of conditions.

It may occur, that aggregation of these analyses may not be efficient in the form Kencse and Mizsey (2010) suggested, because they can be easily substituted with the calculation of enthalpies in several cases. But that is not the case if we regard some additional circumstances. In these examples very simple systems are investigated, costs of operation and GHG emission mainly depend on heating as the other utility is water, which is highly available and cheap. In most plants several possibilities are available for heat integration and several different utilities are also available.

Consequently the costs and GHG Emission also depend on factors other than heating. Thus, in several situations GHG Emission, Total Annual Cost, and enthalpy may not be so strongly correlated.

Exergy Analysis in itself is somewhat different. It is clear that higher complexity of systems makes exergy analysis more useful. Moreover, incorporating in an aggregated index has huge advantages. Including more heat exchanging temperatures in the analysis can add some to the later value of the system. A scheme that has a more efficient core process (*Case #1*) has better chances for integration if it becomes possible with another process later.

Chapter 4

Process Control Investigations

4.1 Introduction

As a part of the process design, the process control also have to be elaborated. Dynamic simulation is available to the engineers of today, and it could be seen in the literature review, that this type of simulation delivers more relevant information about the modeled system. Thus, dynamic behaviour of the possible process design alternatives is investigated in this work and steady-state simulations are not considered.

In this work, SISO/decentralised controller structure is chosen, as it has many advantages over centralised controls, as detailed in Section 2.5. For decentralised control, the control structure have to be designed, i.e., the controlled and Manipulated Variables have to be chosen.

The goal of this study is to verify the method, based on the desirability function, that simplifies dynamic investigation of systems for control structure design. Time Domain simulation is the most reliable tool for this purpose, and these simulations are considered as the reference to which the Frequency Domain results have to be compared. However, Frequency Domain simulations and indicators may be just as good for this purpose if several different indicators are used together.

4.2 Dynamic Investigations

To study dynamic behaviour not only Time Domain, but Frequency Domain investigations can also be used. Such investigations are faster, simpler, and more automatic than modelling in Time Domain (Horváth and Mizsey 2010). However, the success is not guaranteed, the debate on the usability of Control Performance Indicators shows that. Gross et al. (1998) used steady-state RGA and singular values for variable pairing and compared the results with time domain simulations, and found that results in different domains are not coherent. In this study, however, not steady-state but dynamic indicators are used, which describes dynamic behaviour of disturbances better. Another problem is the multitude of indicators. While in Time Domain the summarised behaviour is seen in integral errors, in Frequency Domain quantify different indicators different properties. Thus, in different cases certain indicators can predict the Time Domain behaviour, other indicators can not. To overcome these problems, all widely used indicators are calculated at the same time.

Calculation of all indicators at the same time, however, does not solve all problems that arise. Having more indicators can make greater confusion than

using only one. With multiple characteristics to be optimised, without having methods to transform properties to costs and income the desirability function can help. In this way the modified version on the methodology of Kencse and Mizsey (2010) is used to get consistent results. They proved that multi-criteria evaluation of process alternatives is advantageous and a method can be applied for the ranking of design alternatives based on an indicator number, i.e., the desirability function. They also used it for controllability evaluation purposes (Kencse 2009), but not for variable pairing. In this chapter the most advanced form of indicators are tested and verified for variable pairing: the most popular indicators together, derived from dynamic simulations. This method (Figure 4.1) is the most complex compared to those found in publications, and advanced with indicators, but still simpler than Time Domain simulations. It is described in the following.

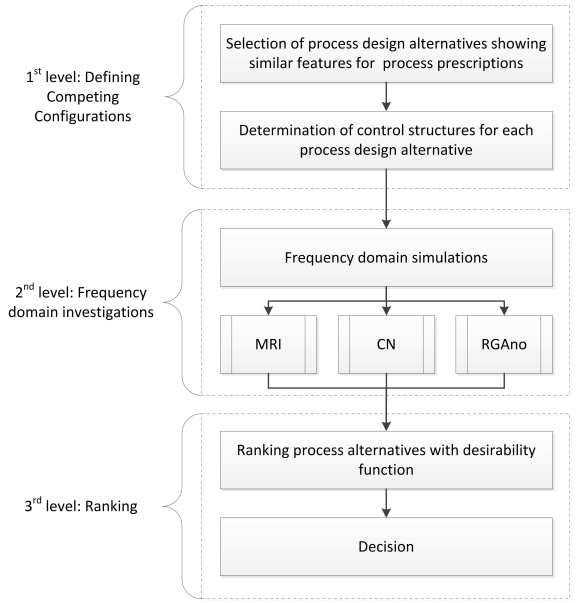


Figure 4.1: Methodology for Advanced Frequency Domain Evaluation

4.2.1 Selection of Controlled and Manipulated Variables

For control purposes independent variables are used. The degree of freedom shows how many independent variables a system has. The first step of the analysis is the selection of the controlled and Manipulated Variables for the investigated systems. A single distillation column has 5 independent variables that have to be controlled. Thus, a distillation column with two products is a 5×5 system, that means 5 Controlled Variables controlled by 5 Manipulated Variables. The Controlled Variables are usually liquid levels in the condenser and in the reboiler, pressure, and compositions (distillate and bottoms product). Since the levels and pressure must always be controlled to ensure stable operation, the level and pressure loops — the so called material balance loops — are designed first (Skogestad, Lundström, et al. 1990). Then, in the next step, the composition control loops can be designed for the distillation column (2×2). This is called inherent decomposition, and it is based on the fact that material balance control loops are much faster than composition control. Consequently, in this research the focus is only on the composition control loops, that have more importance in the control due to their relatively high time constant.

4.2.2 Calculation of the Control Performance Indicators in the Frequency Domain

Controllability Analysis is carried out by calculating the transfer function matrices ($\underline{\underline{G}}(i\omega)$) for open-loop control systems based on the work of Gábor and Mizsey (2008). These transfer function matrices are subjected to singular value decomposition (SVD, Klema and Laub (1980)). Based on SVD, and transfer function matrices Control Performance Indicators can be calculated. In this work I used Morari Resiliency Index (MRI), Condition Number (CN) and a derivative of the Relative Gain Array matrix: RGA-number (RGAno). These Control Performance Indicators are used to predict the degree of directionality and the level of interactions in the system. Analysis is carried out in the Frequency Domain, to calculate frequency dependent indicators, which yields additional information about the investigated system (Skogestad, Jacobsen, et al. 1990). It is important to note that Control Performance Indicators can be calculated in a wide range of frequencies, but from controllability point of view the critical frequencies are the most important. Critical frequencies are those that can be calculated from the time constant of the control loop (Eq. (4.1)). To determine the time constant, a step-disturbance is introduced to the system with the control loop open, while the CV of the loop is monitored. From the

resulting response curve of the CV, control parameters and time constant can be calculated.

$$\omega_{crit} = \frac{2\pi}{\tau_{ol}} \qquad \left[\frac{rad}{s}\right] \tag{4.1}$$

4.2.3 Aggregation of Control Performance Indicators, Ranking

Last step of the methodology is to calculate desirability of each case and to make the decision based on the desirability function ($D - fct$). Each indicator is transformed into individual desirability values, ds that are part of 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. 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. (2.10), and this makes the easy ranking of the process alternatives possible.

High value of $D - fct$ shows that all d_k are toward the target value that indicates the most adequate process alternative. 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 subjected to the detailed engineering design as the next step of the process design project.

4.2.4 Using Desirability Functions with Control Performance Indicators in the Frequency Domain

Overall desirability function $D - fct$ is defined as the geometric average of individual desirability functions. In this study, weight factors are not used, for the reason mentioned at the introduction of the desirability function (Section 2.7). Control Performance Indicators describe the transfer matrices of the process and their values can be classified immediately independently of the process, therefore the only task is to create functions that convert desirable indicator values to d values close to 1 meanwhile discriminate worse indicator values by assigning values close to 0 to them.

Indicators in some cases can also have very high or low values; therefore, a linear function is not eligible to transform these values in every possible case.

Properly chosen exponential functions can, however, transform indicators to fit in the [0..1] interval. Exponential functions are even better to make distinction between indicators in the desired range. Other modifications of the exponential base functions are constructed empirically to fulfil the requirements of the given Control Performance Indicators. The applied individual desirability functions have the following specification:

a) 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 said to be ill-conditioned. Between 10 and 100 it can be both good or poorly conditioned depending on the investigated structure (Seborg et al. 2004). 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 because of its large CN. The chosen d_{CN} function which describes the previously mentioned criteria has the form of Eq. (4.2)

$$d_{CN} = \exp(-(a + b \times CN)) \tag{4.2}$$

According to previous investigations values $a = 1.11084 \times 10^{-4}$ and $b = 6.967 \times 10^{-3}$ are a good choice to transform CNs to values (Kencse 2009).

b) Large MRI value predicts resilient 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 Eq. (4.3). 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.

$$d_{MRI} = 1 - \exp(-10 \times MRI)) \tag{4.3}$$

c) Small values of RGAno indicate preferable variable pairings with less interaction between variables. Therefore, the minimization of this individual response is advantageous. The chosen function d_{RGAno} Eq. (4.4) favours RGAno values lower than 1 and its value abruptly decrease at higher values than 1.

$$d_{RGAno} = \exp(-\frac{RGAno}{10}) \tag{4.4}$$

4.2.5 Load Rejection Analysis in Time Domain

Control loops in Time Domain are closed and tuned. The PI controllers are tuned with the Ziegler-Nichols method using the automatic tuning tool of Aspen Dynamics. Performance of the control loops is evaluated by Load Rejection Analysis that is based on the Integral Absolute Error: (IAE, (Eq. (4.5)).

$$IAE = \int_0^\infty |e(t)|\, dt \tag{4.5}$$

4.2.6 Defining Systems to Satisfy Specifications

Before the analysis takes place, the possible design alternatives have to be elaborated as usual. The models have to meet the specifications to produce the desired products. This means steady-state short-cut calculations and rigorous steady-state modelling. The steady-state model is then specified more precisely, and transformed into a dynamic model, which is needed for this type of analysis. Product specifications are the same in every case.

Controlled Variables are product compositions for the reasons detailed earlier, possible Manipulated Variables can be seen in Figure 4.2. First, possible variable pairings can be filtered by a rule-of-a-thumb: the best Manipulated Variables will be those that are "close" to the controlled variable. This makes sense, because otherwise the effect of manipulation reaches the controlled property later, causing lag which surely is worse controllable. Following this discipline, distillation composition should not be controlled by reboiler heat duty for example.

Investigated control structure names denote their corresponding manipulated variables for distillate composition and bottoms composition respectively. For example RB means that distillate composition is controlled by reflux ratio, and bottoms product composition is controlled by bottoms flow rate. Other structures are analogues to this notation (Table 4.1). The following pairs are investigated: RB, RQ, DQ, LB and LQ. Feed stream is equimolar mixture of two components, product purity is 95% in every case (Table 4.2). Three types of binary zeotropic mixtures are separated:

- benzene–toluene
- n-heptane–n-hexane
- ethanol–propanol

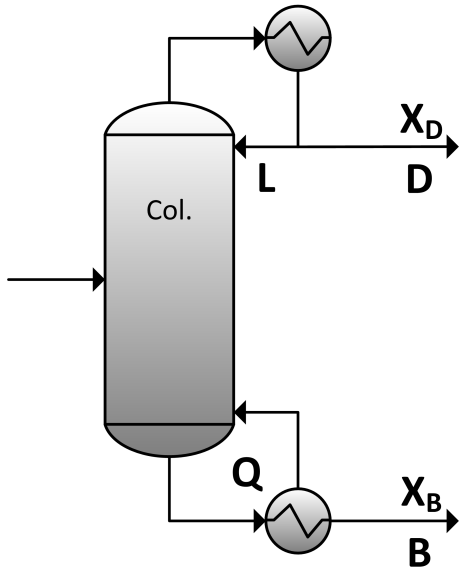


Figure 4.2: Possible Controlled and Manipulated Variables of a Single Column

4.3 Software Background

The steady-state model is built in Aspen Plus software. It is then exported to Aspen Dynamics, where the open loop matrices of the state space model of the investigated system are obtained using the built-in control design interface (CDI). The closed-loop dynamic simulations are also performed in this software. The matrices of the state-space model are then processed with MATLAB software suite. In parallel, open-loop simulations in Time Domain are also carried out to verify Frequency Domain results, and to calculate the eigenfrequency/critical frequency of control loops. They are calculated from the time constant of the loop responses to disturbance (Eq. (4.1)).

Table 4.1: MVs of CVs (x_D and x_B) for the investigated pairings (variable names as in Figure 4.2)

	RQ	**RB**	**LQ**	**LD**	**LB**
x_D	R	R	L	L	L
x_B	Q	B	Q	D	B

Table 4.2: compositions of the separated mixtures of variable pairing investigations

Mixture	Comp.1	Comp.2	Feed x_1	Dist. x_1	Bott. x_1
aromatic	benzene	toluene	0.5	0.95	0.05
apolar	n-pentane	n-hexane	0.5	0.95	0.05
polar	ethanol	propanol	0.5	0.95	0.05

4.4 Results

4.4.1 Frequency Domain Results

After estimating time constants of the open loop dynamic load rejection for an individual process, critical frequencies are found to be in the range of 7.29×10^{-4} and $5.85 \times 10^{-3} rad/s$ in the Frequency Domain. All indicators are constant in this range; thus, the corresponding indicators are easy to read. Results are summarised in Table 4.3. (High MRI, low CN and low RGAno values are better.) Detailed results can be seen in Appendix **??**.

MRI values show the same situation for all mixtures: DQ structure has the highest value; all other structures have their MRI values close to each other, significantly lower than in the case of the DQ structure. CN values generally are all acceptable, showing good controllability. LQ is the only structure, the value of which exceeds 10, but only in one case being significantly higher than 10. For all mixtures DQ structure has the lowest values and LQ has the highest. RGAnos also present results showing similar properties. For all mixtures RB structure has the lowest value, while LQ has the highest. This one is the only indicator predicting worse controllability of DQ than most of the other structures, because DQ structure has relatively high RGAno values.

It is clear, that the three Control Performance Indicators deliver results that do not support each other unquestionably. MRI and CN ranks have same tendencies, but that is no surprise, since they share a common origin, i.e., the singular value. As soon as we compare them to the RGAno-s, we cannot point similarities out. These facts encourage us to make an attempt to aggregate the different indicators with the desirability function. The results speak for themselves: for all three mixtures the rank is the same. The best controllable structure — with the highest $D - fct$ values — is DQ. It is followed by LB, RB, RQ in this order, and finally the worst controllable pairing is LQ.

4.4.2 Time Domain results

For comparison, Time Domain simulations are also carried out for both feed flow rate load rejection and feed composition load rejection.

In the case of load rejection calculations the integral absolute errors of the two composition control loops are summarised to be able to easily compare the different structures. A step disturbance is applied to the feed and from the settling characteristics the time constant is calculated. 1% load disturbance is applied in the feed flow rate and feed composition.

Results can be seen in Table 4.4. In every case RQ earns first place in all cases with the lowest IAE values meanwhile DQ is the worst with IAE an order of magnitude bigger than that of the better controllers.

LQ is the worst controller structure according to the Frequency Domain results, however, in Time Domain, in many cases it has one of the lowest values meaning good control characteristics. IAE values of LQ structure are lower in all cases than that of the DQ's.

4.4.3 Comparison of Results From Different Domains

The conclusion is that MRI and CN indicators fail to predict the closed loop behaviour in Time Domain. RGAno is the only indicator, that does not show DQ as a good control structure, however, it also proves to be inappropriate, since it suggests that RB is an appropriate control structure. RB, in fact, is ranked third at best in Time Domain simulations. According to RGAno, LQ should perform worse than the majority of alternatives, meanwhile Time Domain simulations show good controllability with this pairing. Indicators suggested that DQ is the best controller structure; thus, we would expect the short control time and small overshoot. Figure 4.3 shows the load rejection of the DQ structure together with LQ, that proved to be inferior in Frequency Domain. The results show that DQ

eliminates load much slower and with a much higher overshoot. This experience contradicts the Frequency Domain results thoroughly. According to these results it is quite clear, that the performance of controllers in different domains do not show any similarities.

Last possibility could be: to take advantage of weighing factors in the desirability function or to modify d functions to give more weight to the indicator that shows ranks closer to Time Domain ranks. Unfortunately no weighing strategy would emphasise that DQ configuration is hardly controllable.

Results show that investigation of Control Performance Indicators in Frequency Domain for the sake of ranking is not able to deliver acceptable results.

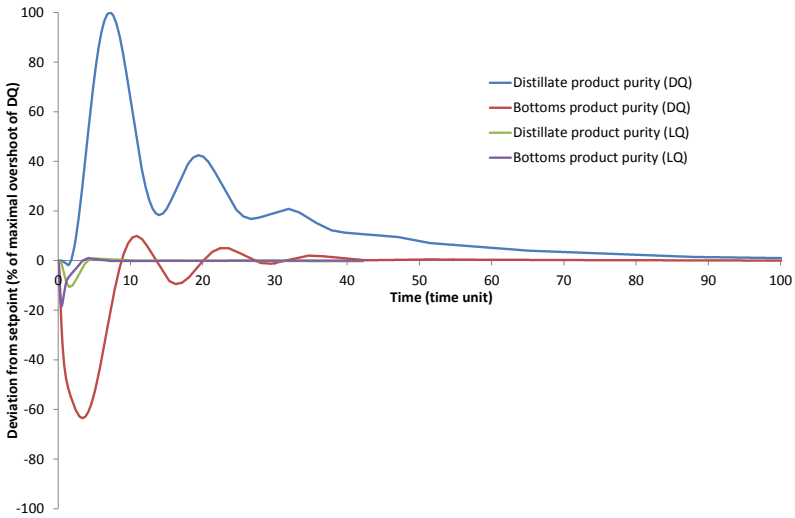


Figure 4.3: Product Composition Deviation from Setpoint in Case of DQ and LQ Structures After Step Change in Feed Composition

4.5 Conclusions of Control Structure Design Investigations

Results of Frequency Domain simulations are almost similar to each other, some small differences can be pointed out, but otherwise the ranks of the control structures generally show the same tendencies. Comparing the Frequency Domain and Time Domain results it can be seen, that Frequency Domain results do not deliver the same result as Time Domain investigations, even the aggregated form based on the application of the overall desirability function is ineligible to replace Time Domain investigations. Such replacement, actually, could have made the control structure design problem much easier and simpler. However, this conclusion of ours is in full agreement with Gross et al. (1998) and shows why the usage of Frequency Domain indicators has not been accepted universally, like mentioned by Skogestad, Lundström, et al. (1990). Despite the most advanced and dynamic modelingit cannot compete with Time Domain.

In our case the DQ structure — which is the best controllable according to frequency-domain results — proves to be almost useless in the dynamic simulations. Meanwhile LQ is at the end of the rank list in the frequency domain, however, in many cases in Time Domain it is one of the best performing structures. RQ structure is undoubtedly the best control structure in time domain, but in the Frequency Domain this excellent behaviour is not predicted.

On the contrary to Kencse and Mizsey (2010) who found Frequency Domain analysis useful for the selection of the best controllable process design alternative, it can now be declared that Frequency Domain examinations, even with the application of the overall desirability function, are not able to replace Time Domain simulations when used for control structure design of a single distillation scheme.

Table 4.3: Frequency Domain Results and Ranks of Different Control Structures for Variable Pairing

benzene–toluene

	DQ	**LB**	**RB**	**RQ**	**LQ**
MRI	0.502	0.179	0.152	0.149	0.172
CN	1.34	4.66	6.42	7.69	11.81
RGAno	2.19	1.17	0.51	0.85	3.97
$D-fct$	0.925	0.895	0.892	0.877	0.797
Rank	I	II	III	IV	V

ethanol–propanol

	DQ	**LB**	**RB**	**RQ**	**LQ**
MRI	0.310	0.147	0.131	0.124	0.133
CN	1.97	5.45	6.81	8.30	20.54
RGAno	2.01	1.72	1.20	3.04	12.78
$D-fct$	0.917	0.854	0.852	0.789	0.562
Rank	I	II	III	IV	V

***n*-pentane–*n*-hexane**

	DQ	**LB**	**RB**	**RQ**	**LQ**
MRI	0.560	0.193	0.160	0.158	0.186
CN	1.18	4.51	6.55	6.44	8.22
RGAno	2.00	1.04	0.29	0.34	2.15
$D-fct$	0.932	0.907	0.905	0.902	0.863
Rank	I	II	III	IV	V

Table 4.4: IAE Values and Ranks of Different Control Structures for Variable Pairing

benzene–toluene

		composition 1% disturbance			
Control structure	RQ	LQ	LB	RB	DQ
$IAE_{x_D} + IAE_{x_B}$	2.06×10^{-5}	3.73×10^{-5}	4.92×10^{-5}	1.41×10^{-4}	1.96×10^{-3}
		feed flow rate 1% disturbance			
Control structure	RQ	LB	RB	LQ	DQ
$IAE_{x_D} + IAE_{x_B}$	3.86×10^{-5}	6.73×10^{-5}	1.19×10^{-4}	1.68×10^{-4}	1.99×10^{-3}
Rank	I	II	III	IV	V

ethanol–propanol

		composition 1% disturbance			
Control structure	RQ	LQ	RB	LB	DQ
$IAE_{x_D} + IAE_{x_B}$	1.61×10^{-5}	2.23×10^{-5}	3.55×10^{-4}	3.01×10^{-3}	6.20×10^{-3}
		feed flow rate 1% disturbance			
Control structure	RQ	LQ	RB	LB	DQ
$IAE_{x_D} + IAE_{x_B}$	2.90×10^{-5}	1.45×10^{-4}	3.20×10^{-4}	2.84×10^{-3}	6.21×10^{-3}
Rank	I	II	III	IV	V

***n*-pentane–*n*-hexane**

		composition 1% disturbance			
Control structure	RQ	LQ	LB	RB	DQ
$IAE_{x_D} + IAE_{x_B}$	2.39×10^{-5}	3.13×10^{-5}	4.47×10^{-5}	1.22×10^{-4}	1.26×10^{-3}
		feed flow rate 1% disturbance			
Control structure	RQ	LB	RB	LQ	DQ
$IAE_{x_D} + IAE_{x_B}$	4.21×10^{-5}	4.73×10^{-5}	9.70×10^{-5}	1.05×10^{-4}	1.37×10^{-3}
Rank	I	II	III	IV	V

Chapter 5

Major New Results

Thesis 1

I elaborated a method in which exergy analysis of a system should be carried out with dual boundaries for the sake of the determination of the maximal exergy saving potential that can be achieved by better integration to other processes. I also proved that this method, the dual exergy analysis, gives an insight into the thermodynamic flexibility of separation systems.

Thesis 2

I elaborated the concept of the ideal background heat cascade that can source and sink any amount of heat at any temperature. I proved that the optimal integration of the investigated process to this cascade defines the core process that involves only the necessary exergy losses.

Thesis 3

I proved that the exergy analysis of the core process is not sensitive to changes in ambient temperatures, but in other cases difference in ambient temperatures can causes change in thermodynamic efficiency ranks.

Thesis 4

I proved that sensitivity of thermodynamic efficiency to product purity prescriptions is different in case of different distillation schemes.

Thesis 5

I proved that backwards heat integration of distillation columns decreases thermal efficiency, compared to cases when the heat integration can be solved outside of the distillation system without increasing pressures.

Thesis 6

I proved that frequency domain controllability indices (CN, MRI, RGAno) cannot be used for the design of the best control structure of an individual rectifi-

cation system, neither individually, nor in an aggregated form; therefore, load rejection investigations in the time domain should be applied to complete such a design task.

List of Figures

List of Tables

Publications

Articles

Haragovics, Máté, Hajnalka Kencse, and Péter Mizsey (2012). "Applicability of Desirability Function for Control Structure Design in the Frequency Domain". In: *Industrial & Engineering Chemistry Research* 51.49. (**IF=2.206**), pp. 16007–16015. DOI: 10.1021/ie300973b.

Haragovics, Máté and Péter Mizsey (2012c). "Exergy Analysis of Multicomponent Distillation Systems for Efficiency Ranking". In: *Chemical Engineering Transactions* 29. DOI: 10.3303/CET1229058.

— (2012d). "Ranking of rectification structures separating quaternary mixtures with exergy analysis". In: *Periodica Polytechnica: Chemical Engineering* 56.1. (**IF=0.217**), pp. 31–35. DOI: 10.3311/pp.ch.2012-1.04.

— (2014a). "A novel application of Exergy Analysis: lean manufacturing tool to improve energy efficiency and flexibility of hydrocarbon processing". In: *Energy*. Accepted, (**IF=4.159**).

— (2014b). "Complex evaluation of multicomponent distillation systems: exergy, emission, and costs". In: *International Journal of Exergy*. Under acceptance, (**IF=0.847**).

Posters

Haragovics, Máté, Hajnalka Kencse, and Péter Mizsey (2010). "Frekvenciavizsgálatok alkalmazhatósága desztillációs oszlopok szabályozhatóságának megállapítására". In: *Oláh György Doktori Iskola konferenciája 2010*. Budapest, HU.

Haragovics, Máté and Péter Mizsey (2012b). “Exergy Analysis of Multicomponent Distillation Systems for Efficiency Ranking”. In: *PRES 2012*. Praha, CZ.

— (2013). “Exergy analysis of multicomponent distillation systems for efficiency ranking”. In: *Oláh György Doktori Iskola konferenciája 2013*. Budapest, HU.

Mizsey, Péter, Tamás Benkő, Edit Cséfalvay, Máté Haragovics, Katalin Koczka, József Manczinger, Tibor Nagy, Viktor Pauer, András Tóth, and Nóra Valentínyi (2011). “Zöld technológiák alkalmazása a fenntartható fejlődésben”. In: *A mi világunk kémiája szimpózium*. Budapest, HU.

— (2012). “Zöld technológiák alkalmazása a fenntartható fejlődésben”. In: *Jövő Hídja*. Budapest, HU.

Presentations

Haragovics, Máté and Péter Mizsey (2011). “Applicability of desirability function for control structure design in frequency domain”. In: *Interfaces ’11*. Sopron, HU.

— (2012a). “Exergy analysis of distillation structures separating quaternary mixtures”. In: *Műszaki Kémiai Napok ’12*. Veszprém, HU: Pannon Egyetemi Kiadó, p. 86.

References

Adiche, Chafika and Alfons Vogelpohl (2011). "Short-cut methods for the optimal design of simple and complex distillation columns". In: *Chemical Engineering Research and Design* 89.8, pp. 1321–1332.

Alcántara-Ávila, Jesús Rafael, Julián Cabrera-Ruiz, Juan Gabriel Segovia-Hernández, Salvador Hernández, and Ben-Guang Rong (2008). "Controllability analysis of thermodynamically equivalent thermally coupled arrangements for quaternary distillations". In: *Chemical Engineering Research and Design* 86.1, pp. 23–37.

Bandyopadhyay, Santanu (2007). "Thermal Integration of a Distillation Column Through Side-Exchangers". In: *Chemical Engineering Research and Design* 85.1, pp. 155–166.

Bandyopadhyay, Santanu, James Varghese, and Vikas Bansal (2010). "Targeting for cogeneration potential through total site integration". In: *Applied Thermal Engineering* 30.1, pp. 6–14.

Bezzo, F., R. Bernardi, G. Cremonese, M. Finco, and M. Barolo (2004). "Using Process Simulators for Steady-State and Dynamic Plant Analysis: An Industrial Case Study". In: *Chemical Engineering Research and Design* 82.4, pp. 499–512.

Birky, G., T. McAvoy, and B. Tyreus (1989). "DICODE-An Expert System for Designing Distillation Column Controls". English. In: *Proceedings of the 1989 American Control Conference, Vols. 1-3.* American Control Conference. 8th Annual American Control Conf on Automation and Control, Pittsburgh, PA, JUN 21-23, 1989. Green Valley: Amer Automatic Control Council, 95–100.

BP (2014). *Statistical Review of World Energy.* Report. BP.

Bristol, E. (1966). "On a new measure of interaction for multivariable process control". In: *Automatic Control, IEEE Transactions on* 11.1, pp. 133–134.

Climate Change, Intergovernmental Panel on (2007). *Fourth Assessment Report: Climate Change 2007: The AR4 Synthesis Report.* Geneva: IPCC.

Derringer, G. and R. Suich (1980). "Simultaneous optimization of several response variables". In: *Journal of Quality Technology* 12, pp. 214–219.

Dhole, Vikas R. and Bodo Linnhoff (1993). "Total site targets for fuel, cogeneration, emissions, and cooling". In: *Computers & Chemical Engineering* 17, Supplement 1, S101–S109.

Douglas, J. M. (1988). *Conceptual Design of Chemical Processes*. New York: McGraw-Hill.

Emtir, M., E. Rév, P. Mizsey, and Z. Fonyó (1999). "Comparison of integrated and coupled distillation schemes using different utility prices". In: *Computers & Chemical Engineering* 23, Supplement, S799–S802.

Feng, X. and X. X. Zhu (1997). "Combining pinch and exergy analysis for process modifications". In: *Applied Thermal Engineering* 17.3, pp. 249–261. ISSN: 1359-4311. DOI: http://dx.doi.org/10.1016/S1359-4311(96)00035-X.

Fonyó, Z. (1974a). "Thermodynamic Analysis of Rectification - 1. Reversible Model of Rectification". In: *International Chemical Engineering* 14.1, pp. 18–27.

— (1974b). "Thermodynamic Analysis of Rectification - 2. Finite Cascade Models". In: *International Chemical Engineering* 14.2, pp. 203–210.

Gábor, M. and P. Mizsey (2008). "A methodology to determine controllability indices in the frequency domain". In: *Industrial & Engineering Chemistry Research* 47.14, pp. 4807–4816.

Gadalla, M., L. Jimenez, Z. Olujic, and P. J. Jansens (2007). "A thermo-hydraulic approach to conceptual design of an internally heat-integrated distillation column (i-HIDiC)". In: *Computers & Chemical Engineering* 31.10, pp. 1346–1354.

Gross, F., E. Baumann, A. Geser, D. W. T. Rippin, and L. Lang (1998). "Modelling, simulation and controllability analysis of an industrial heat-integrated distillation process". In: *Computers & Chemical Engineering* 22.1-2, pp. 223–237.

Grossmann, Ignacio E., Pío A. Aguirre, and Mariana Barttfeld (2005). "Optimal synthesis of complex distillation columns using rigorous models". In: *Computers & Chemical Engineering* 29.6, pp. 1203–1215.

Guo, Zeng-Yuan, Hong-Ye Zhu, and Xin-Gang Liang (2007). "Entransy-A physical quantity describing heat transfer ability". In: *International Journal of Heat and Mass Transfer* 50.13, pp. 2545–2556. ISSN: 0017-9310. DOI: http://dx.doi.org/10.1016/j.ijheatmasstransfer.2006.11.034.

Hackl, Roman, Eva Andersson, and Simon Harvey (2011). "Targeting for energy efficiency and improved energy collaboration between different companies using total site analysis (TSA)". In: *Energy* 36.8, pp. 4609–4615.

Hackl, Roman and Simon Harvey (2013). "Applying exergy and total site analysis for targeting refrigeration shaft power in industrial clusters". In: *Energy* 55, pp. 5–14.

Haggblom, K. E. (1997). "Control structure analysis by partial relative gains". In: *Proceedings of the 36th Ieee Conference on Decision and Control, Vols 1-5*. 36th IEEE Conference on Decision and Control DEC 10-12, 1997 SAN DIEGO, CA 0-7803-4187-2, pp. 2623–2624.

Häggblom, K. E. (1997). "Analytical approach to evaluation of distillation control structures by frequency-dependent relative gains". In: *Computers & Chemical Engineering* 21.12, pp. 1441–1449.

El-Halwagi, Mahmoud M. and Vasilios Manousiouthakis (1989). "Synthesis of mass exchange networks". In: *AIChE Journal* 35.8, pp. 1233–1244. ISSN: 1547-5905. DOI: 10.1002/aic.690350802.

Harrington, E.C. (1965). "The desirability function". In: *Industrial Quality Control* 21, pp. 494–498.

Horváth, M. and P. Mizsey (2010). "Decomposability Investigations for Control Structure Design of Recycle Systems in the Frequency-domain". In: *Revista De Chimie* 61.7, pp. 696–701.

Huang, K., L. Shan, Q. Zhu, and J. Qian (2008). "A totally heat-integrated distillation column (THIDiC) - the effect of feed pre-heating by distillate". In: *Applied Thermal Engineering* 28.8-9, pp. 856–864.

Kencse, Hajnalka (2009). "Complex evaluation methodology for energy-integrated distillation columns". PhD thesis. George Oláh Doctoral School.

Kencse, Hajnalka and Péter Mizsey (2009). "Comparative Study of Energy-Integrated Distillation Systems Based on Exergy Analysis and Greenhouse Gas Emissions". In: *Revista De Chimie* 60.10, pp. 1047–1052.

— (2010). "Methodology for the Design and Evaluation of Distillation Systems: Exergy Analysis, Economic Features and GHG Emissions". In: *Aiche Journal* 56.7, pp. 1776–1786.

Khoshgoftar Manesh, M. H., H. Ghalami, M. Amidpour, and M. H. Hamedi (2013). "Optimal coupling of site utility steam network with MED-RO desalination through total site analysis and exergoeconomic optimization". In: *Desalination* 316, pp. 42–52.

Kiran, B., A. K. Jana, and A. N. Samanta (2012). "A novel intensified heat integration in multicomponent distillation". In: *Energy* 41.1, pp. 443–453.

Klema, V. and A. Laub (1980). "The singular value decomposition: Its computation and some applications". In: *Automatic Control, IEEE Transactions on* 25.2, pp. 164–176.

Klemeš, J., V. R. Dhole, K. Raissi, S. J. Perry, and L. Puigjaner (1997). "Targeting and design methodology for reduction of fuel, power and CO2 on total sites". In: *Applied Thermal Engineering* 17.8, pp. 993–1003.

Klemeš, Jiří Jaromír and Zdravko Kravanja (2013). "Forty years of Heat Integration: Pinch Analysis (PA) and Mathematical Programming (MP)". In: *Current Opinion in Chemical Engineering* 2.4, pp. 461–474. ISSN: 2211-3398. DOI: http://dx.doi.org/10.1016/j.coche.2013.10.003.

Koczka, K. and P. Mizsey (2010). "New area for distillation: wastewater treatment". In: *Periodica Polytechnica-Chemical Engineering* 54.1, pp. 41–45.

Koeijer, Gelein de and Ricardo Rivero (2003). "Entropy production and exergy loss in experimental distillation columns". In: *Chemical Engineering Science* 58.8, pp. 1587–1597.

Linnhoff, B., D.W. Townsend, D. Boland, G.F. Hewitt, B.E.A. Thomas, A.R. Guy, and R.H. Marsland (1982). *A User Guide on Process Integration for the Efficient Use of Energy*. Pergamon Press.

Linnhoff, Bodo and John R. Flower (1978). "Synthesis of heat exchanger networks: I. Systematic generation of energy optimal networks". In: *AIChE Journal* 24.4, pp. 633–642.

Luyben, W. L. (1979). "Introduction and Overview of Distillation Column Control". In: *Workshop Industrial Process Control, Published by AlChE*, pp. 54–58.

— (1989). "The impact of process diversity on distillation column control". In: *Preprints IFAC Symp. DYCORD + 89, Maastricht, Netherlands*, pp. 3–9.

Mao, Wei, Hongzhu Ma, and Bo Wang (2010). "Performance of batch vacuum distillation process with promoters on coke-plant wastewater treatment". In: *Chemical Engineering Journal* 160.1, pp. 232–238. ISSN: 1385-8947. DOI: 10.1016/j.cej.2010.03.053.

Matsuda, Kazuo, Shigeki Tanaka, Masaru Endou, and Tsutomu Iiyoshi (2012). "Energy saving study on a large steel plant by total site based pinch technology". In: *Applied Thermal Engineering* 43, pp. 14–19.

Moran, Michael J. (2011). *Fundamentals of engineering thermodynamics*. 7th Edition. [Hoboken, N.J.]: Wiley. ISBN: 9780470917688 0470917687 9780470495902 0470495901.

Morari, M. (1983a). "Design of resilient processing plants .3. A general framework for the assessment of dynamic resilience". In: *Chemical Engineering Science* 38.11, pp. 1881–1891.

— (1983b). "Flexibility and Resiliency of Process Systems". In: *Computers & Chemical Engineering* 7.4, pp. 423–437.

Murrieta-Duenas, R., R. Gutiérrez-Guerra, J. G. Segovia-Hernández, and S. Hernández (2011). "Analysis of control properties of intensified distillation sequences: Reactive and extractive cases". In: *Chemical Engineering Research and Design* In Press, Corrected Proof.

OMSZ (2013). *Magyarország hőmérsékleti viszonyai*. URL: `http://met.hu/eghajlat/magyarorszag_eghajlata/altalanos_eghajlati_jellemzes/homerseklet/`.

Potoglou, D., A. Kouzeli-Katsiri, and D. Haralambopoulos (2004). "Solar distillation of olive mill wastewater". In: *Renewable Energy* 29.4, pp. 569–579. ISSN: 0960-1481. DOI: `10.1016/j.renene.2003.09.002`.

Razzaghi, K. and F. Shahraki (2007). "Robust control of an ill-conditioned plant using μ-synthesis: A case study for high-purity distillation". In: *Chemical Engineering Science* 62.5, pp. 1543–1547.

Rivero, R., C. Rendón, and S. Gallegos (2004). "Exergy and exergoeconomic analysis of a crude oil combined distillation unit". In: *Energy* 29.12-15, pp. 1909–1927.

Sågfors, M. F. and K. V. Waller (1998). "Multivariable control of ill-conditioned distillation columns utilizing process knowledge". In: *Journal of Process Control* 8.3, pp. 197–208.

Seader, J. D. and Ernest. J. Henley (2006). *Separation Process Principles*. Wiley.

Seborg, Dale E., Thomas F. Edgar, and Duncan A. Mellichamp (2004). "Process Dynamics and Control". In: 2nd. John Wiley & Sons, Inc., pp. 493–497.

Segovia-Hernández, J. G., E. A. Hernández-Vargas, and J. A. Márquez-Munoz (2007). "Control properties of thermally coupled distillation sequences for different operating conditions". In: *Computers & Chemical Engineering* 31.7, pp. 867–874.

Shelley, Mark D. and Mahmoud M. El-Halwagi (2000). "Component-less design of recovery and allocation systems: a functionality-based clustering approach". In: *Computers & Chemical Engineering* 24.9, pp. 2081–2091. ISSN: 0098-1354. DOI: `http://dx.doi.org/10.1016/S0098-1354(00)00578-0`.

Shinskey, F. G. (1979). *Process-control systems : application, design, and tuning*. New York : McGraw-Hill.

— (1984). *Distillation control : for productivity and energy conservation*. New York : McGraw-Hill.

Skogestad, S. (2004). "Control structure design for complete chemical plants". In: *Computers & Chemical Engineering* 28.1-2, pp. 219–234.

Skogestad, S. and I. Postlethwaite (1996). *Multivariable Feedback Control Analysis and Design*. John Wiley & Sons.

Skogestad, Sigurd and K. Havre (1996). "The use of RGA and condition number as robustness measures". In: *Computers & Chemical Engineering* 20.Supplement 2, S1005–S1010.

Skogestad, Sigurd, E. W. Jacobsen, and M. Morari (1990). "Inadequacy of Steady-State Analysis for Feedback-Control - Distillate-Bottom Control of Distillation-Columns". In: *Industrial & Engineering Chemistry Research* 29.12, pp. 2339–2346.

Skogestad, Sigurd, P. Lundström, and E. W. Jacobsen (1990). "Selecting the Best Distillation Control Configuration". In: *Aiche Journal* 36.5, pp. 753–764.

Sun, Jinsheng, Fan Wang, Tingting Ma, Hong Gao, Peng Wu, and Lili Liu (2012). "Energy and exergy analysis of a five-column methanol distillation scheme". In: *Energy* 45.1, pp. 696–703.

Suphanit, B., A. Bischert, and P. Narataruksa (2007). "Exergy loss analysis of heat transfer across the wall of the dividing-wall distillation column". In: *Energy* 32.11, pp. 2121–2134.

Tan, Raymond R. and Dominic C. Y. Foo (2007). "Pinch analysis approach to carbon-constrained energy sector planning". In: *Energy* 32.8, pp. 1422–1429. ISSN: 0360-5442. DOI: http://dx.doi.org/10.1016/j.energy.2006.09.018.

Tóth, András. J., F. Gergely, and P. Mizsey (2011). "Physicochemical treatment of pharmaceutical process wastewater: distillation and membrane processes". In: *Periodica Polytechnica-Chemical Engineering* 55.2, pp. 59–67.

Varbanov, Petar Sabev, Zsófia Fodor, and Jiří Jaromír Klemeš (2012). "Total Site targeting with process specific minimum temperature difference (dTmin)". In: *Energy* 44.1, pp. 20–28.

Vazquez-Castillo, J. A., J. A. Venegas-Sánchez, J. G. Segovia-Hernández, H. Hernández-Escoto, S. Hernández, C. Gutiérrez-Antonio, and A. Briones-Ramírez (2009). "Design and optimization, using genetic algorithms, of intensified distillation systems for a class of quaternary mixtures". In: *Computers & Chemical Engineering* 33.11, pp. 1841–1850.

Wan Alwi, Sharifah Rafidah, Nor Erniza Mohammad Rozali, Zainuddin Abdul-Manan, and Jiří Jaromír Klemeš (2012). "A process integration targeting method for hybrid power systems". In: *Energy* 44.1, pp. 6–10. ISSN: 0360-5442. DOI: http://dx.doi.org/10.1016/j.energy.2012.01.005.

Wang, San-Jang, Chi-Ju Lee, Shi-Shang Jang, and Shyan-Shu Shieh (2008). "Plant-wide design and control of acetic acid dehydration system via heterogeneous azeotropic distillation and divided wall distillation". In: *Journal of Process Control* 18.1, pp. 45–60.

Wang, Y. P. and R. Smith (1994). "Wastewater minimisation". In: *Chemical Engineering Science* 49.7, pp. 981–1006. ISSN: 0009-2509. DOI: http://dx.doi.org/10.1016/0009-2509(94)80006-5.

Womack, James P., Daniel T. Jones, and Daniel Roos (1991). *The Machine That Changed the World: The Story of Lean Production*. New York: HarperCollins. ISBN: 978-0060974176.

Zhang, Xingxing, Kejin Huang, Haisheng Chen, and Shaofeng Wang (2011). "Comparing three configurations of the externally heat-integrated double distillation columns (EHIDDiCs)". In: *Computers & Chemical Engineering* 35.10, pp. 2017–2033.

Zhao, Dongfeng, Jianliang Xue, Shi Li, Hui Sun, and Qing-dong Zhang (2011). "Theoretical analyses of thermal and economical aspects of multi-effect distillation desalination dealing with high-salinity wastewater". In: *Desalination* 273.2, pp. 292–298. ISSN: 0011-9164. DOI: 10.1016/j.desal.2011.01.048.

Zhu, Ping (2008). "An Improved Calculation of the Thermodynamically Based Allocation of Cumulative Exergy Consumption in the Petroleum Distillation Process". In: *Chinese Journal of Chemical Engineering* 16.1, pp. 104–107.

Appendix A

Further Results of Exergy Analysis

Column parameters

In this section the list of the important column parameters are detailed. Values in parentheses refer to parameters of trim heat exchangers in heat integrated systems, while temperatures in red show that those results are not physically feasible, but remained in the group for comparison. In reality those high temperatures would result in hydrocarbon cracking.

Table A.1: Alkane case pressures and stages)

		DS	DS-EP	DS-BHI	SC	SC-OHV
p_1	[bar]	1	1	1	1	1
p_2	[bar]		2.5	2.5		
p_3	[bar]		4.2	4.2		
n_1	[-]	13	13	13	40	40
n_2	[-]	13	13	13		
n_3	[-]	14	14	14		

Table A.2: Aromatic case pressures and stages

		DS	DS-EP	DS-BHI	SC	SC-OHV
p_1	[bar]	1	1	1	1	1
p_2	[bar]		2.5	2.5		
p_3	[bar]		4.2	4.2		
n_1	[-]	39	39	39	120	120
n_2	[-]	39	39	39		
n_3	[-]	42	42	42		

Table A.3: ALK-LP (trim condensers/reboilers in parenthesis)

		DS	DS-EP	DS-BHI	SC	SC-OHV
R_1	[-]	0.22	0.22	0.21	1.79	8.16
R_2	[-]	1.10	1.20	1.23		
R_3	[-]	0.43	0.80	0.82		
$T_{C,1}$	[°C]	40.0	40.0	40.0	40.4	38.4
$Q_{C,1}$	[kW]	-94.2	-94.2	-93.8	-212.5	-682.5
$T_{R,1}$	[°C]	85.4	85.4	(85.3)	116.8	230.8
$Q_{R,1}$	[kW]	248.0	248.0	(70.2)	385.3	850.0
$T_{C,2}$	[°C]	62.1	95.0			
$Q_{C,2}$	[kW]	-178.6	-174.9			
$T_{R,2}$	[°C]	105.5	(141.2)	141.3		
$Q_{R,2}$	[kW]	194.7	265.6	(120.0)		
$T_{C,3}$	[°C]	96.3	154.6			
$Q_{C,3}$	[kW]	-134.8	-146.7			
$T_{R,3}$	[°C]	117.5	177.8	177.8		
$Q_{R,3}$	[kW]	137.7	188.8	190.2		
$T_{PHX,1}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,1}$	[kW]	-14.0	-14.0	-14.0	-14.2	-13.0
$T_{PHX,2}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,2}$	[kW]	-27.6	-47.1	-47.0	-26.9	-33.0
$T_{PHX,3}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,3}$	[kW]	-55.1	-99.1	-99.2	-56.4	-53.7
$T_{PHX,4}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,4}$	[kW]	-76.3	-127.9	-128.0	-75.6	-68.1

Table A.4: ALK-HP results (trim condensers/reboilers in parenthesis)

		DS	DS-EP	DS-BHI	SC	SC-OHV
R_1	[-]	1.20	1.20	1.22	16.00	34.34
R_2	[-]	3.00	5.00	5.14		
R_3	[-]	2.35	6.00	5.90		
$T_{C,1}$	[°C]	36.7	36.7	36.7	36.8	36.6
$Q_{C,1}$	[kW]	-160.3	-160.3	-161.7	-1240.1	-2570.9
$T_{R,1}$	[°C]	89.9	89.9	(89.9)	121.8	781.3
$Q_{R,1}$	[kW]	322.3	322.3	(-143.2)	1421.0	2750.0
$T_{C,2}$	[°C]	67.3	99.8			
$Q_{C,2}$	[kW]	-327.2	-456.1			
$T_{R,2}$	[°C]	108.5	144.3	(144.3)		
$Q_{R,2}$	[kW]	341.9	546.4	(20.5)]		
$T_{C,3}$	[°C]	97.8	155.5			
$Q_{C,3}$	[kW]	-302.2	-544.6			
$T_{R,3}$	[°C]	123.2	183.9	183.8		
$Q_{R,3}$	[kW]	306.5	588.5	580.5		
$T_{PHX,1}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,1}$	[kW]	-12.1	-12.1	-12.1	-12.1	-12.0
$T_{PHX,2}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,2}$	[kW]	-30.8	-50.4	-50.4	-30.1	-30.1
$T_{PHX,3}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,3}$	[kW]	-55.8	-99.3	-99.3	-57.7	-55.0
$T_{PHX,4}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,4}$	[kW]	-82.5	-135.9	-135.9	-80.9	-80.4

Table A.5: ARO-LP (trim condensers/reboilers in parenthesis)

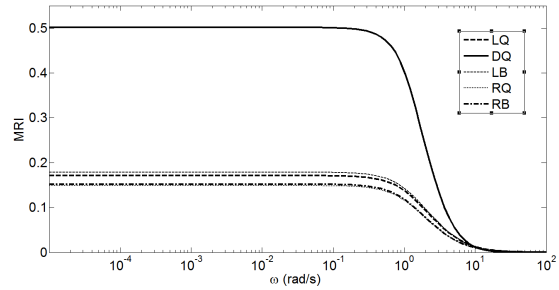
		DS	DS-EP	DS-BHI	SC	SC-OHV
R_1	[-]	0.20	0.20	0.18	2.60	12.14
R_2	[-]	2.20	2.50	2.53		
R_3	[-]	1.00	1.45	1.50		
$T_{C,1}$	[°C]	85.1	85.1	85.3	83.9	81.9
$Q_{C,1}$	[kW]	-108.2	-108.2	-106.3	-315.6	-1134.6
$T_{R,1}$	[°C]	123.9	123.9	(123.7)	146.6	453.9
$Q_{R,1}$	[kW]	313.1	313.1	(0.7)	533.7	1350.0
$T_{C,2}$	[°C]	102.6	138.5			
$Q_{C,2}$	[kW]	-298.8	-308.0			
$T_{R,2}$	[°C]	141.1	179.6	(179.6)		
$Q_{R,2}$	[kW]	310.5	390.2	(168.9)		
$T_{C,3}$	[°C]	136.2	199.7			
$Q_{C,3}$	[kW]	-202.7	-219.2			
$T_{R,3}$	[°C]	146.5	211.4	211.4		
$Q_{R,3}$	[kW]	203.3	257.4	261.8		
$T_{PHX,1}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,1}$	[kW]	-28.1	-28.1	-28.3	-27.1	-25.8
$T_{PHX,2}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,2}$	[kW]	-39.2	-57.1	-56.8	-40.7	-46.8
$T_{PHX,3}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,3}$	[kW]	-69.3	-112.4	-112.2	-69.6	-66.8
$T_{PHX,4}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,4}$	[kW]	-81.4	-129.6	-129.7	-81.5	-76.9

Table A.6: ARO-HP *(trim condensers/reboilers in italics)*

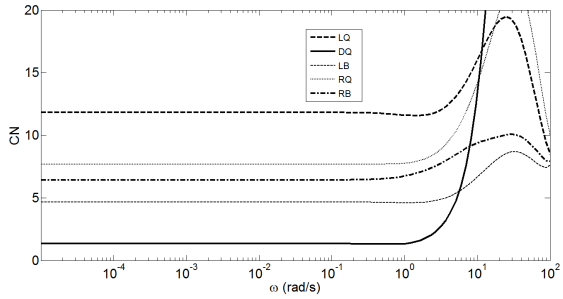
		DS	DS-EP	DS-BHI	SC	SC-OHV
R_1	[-]	1.17	1.17	1.19	40.00	78.80
R_2	[-]	3.30	5.20	4.95		
R_3	[-]	3.50	5.00	5.06		
$T_{C,1}$	[°C]	80.1	80.1	80.0	80.1	80.1
$Q_{C,1}$	[kW]	-184.3	-184.3	-185.6	-3483.1	-6777.6
$T_{R,1}$	[°C]	129.3	129.3	(129.3)	150.5	2034.1
$Q_{R,1}$	[kW]	397.5	397.5	(-163.1)	3706.3	7000.0
$T_{C,2}$	[°C]	110.9	146.9			
$Q_{C,2}$	[kW]	-398.5	-539.6			
$T_{R,2}$	[°C]	142.9	181.6	(181.6)		
$Q_{R,2}$	[kW]	407.0	620.3	(101.8)		
$T_{C,3}$	[°C]	136.5	199.7			
$Q_{C,3}$	[kW]	-448.7	-528.3			
$T_{R,3}$	[°C]	150.6	215.9	215.9		
$Q_{R,3}$	[kW]	450.1	567.7	572.9		
$T_{PHX,1}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,1}$	[kW]	-24.6	-24.6	-24.6	-24.6	-24.6
$T_{PHX,2}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,2}$	[kW]	-44.5	-63.2	-55.9	-44.4	-45.3
$T_{PHX,3}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,3}$	[kW]	-68.6	-111.0	-111.0	-68.8	-67.3
$T_{PHX,4}$	[°C]	10.0	10.0	10.0	10.0	10.0
$Q_{PHX,4}$	[kW]	-86.6	-136.7	-136.8	-86.5	-86.2

Appendix B

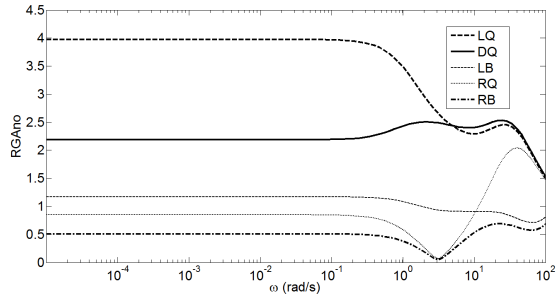
Further Results of Process Control



(a) MRI

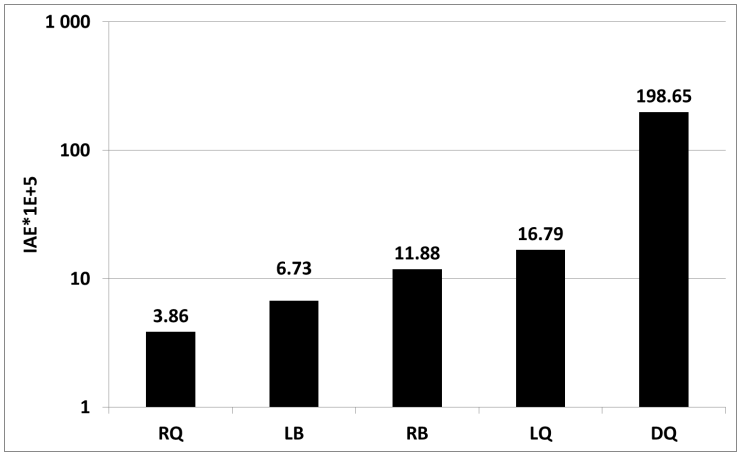


(b) CN

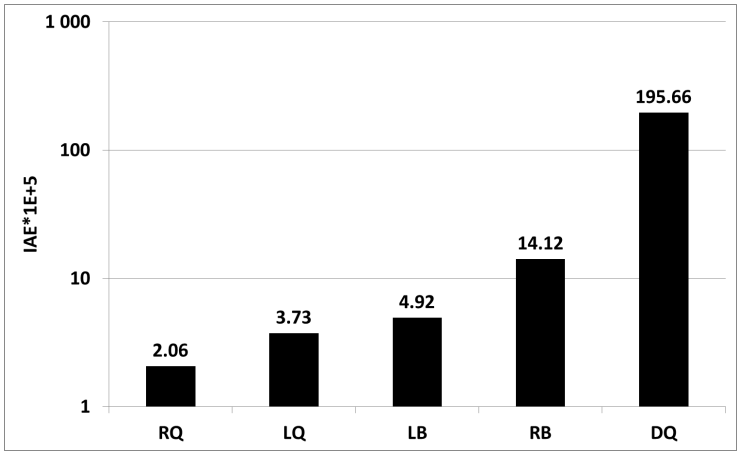


(c) RGAno

Figure B.1: Frequency Domain Indices of Benzene–Toluene Column

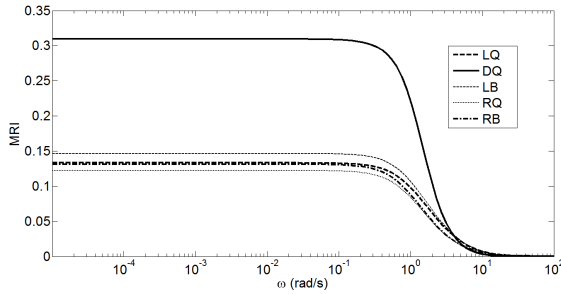


(a) flow rate disturbance

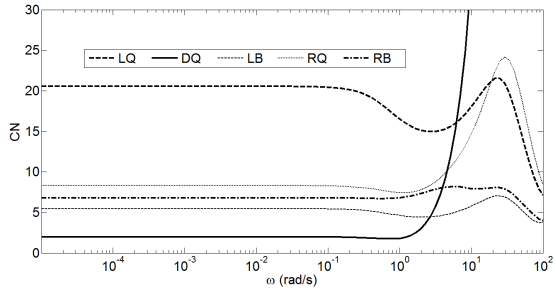


(b) composition disturbance

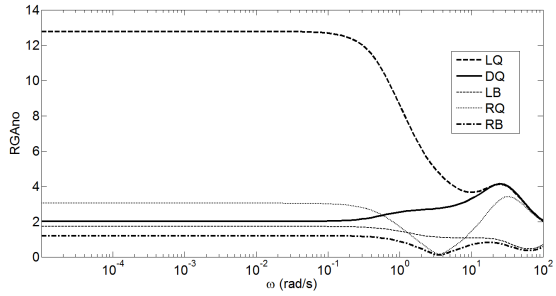
Figure B.2: IAE of Benzene–Toluene Column



(a) MRI

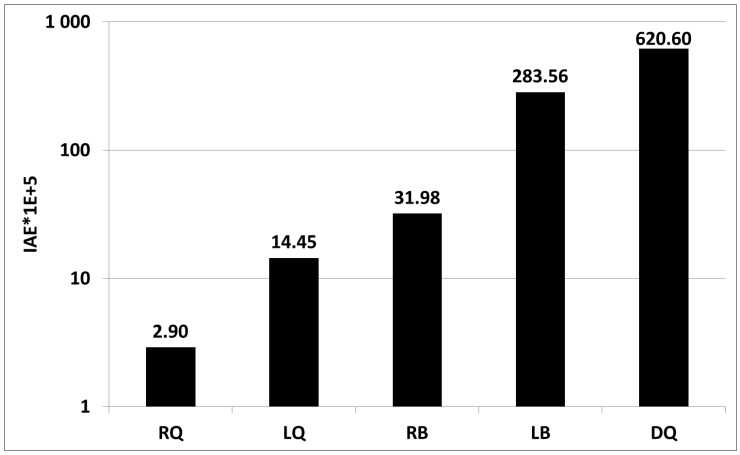


(b) CN

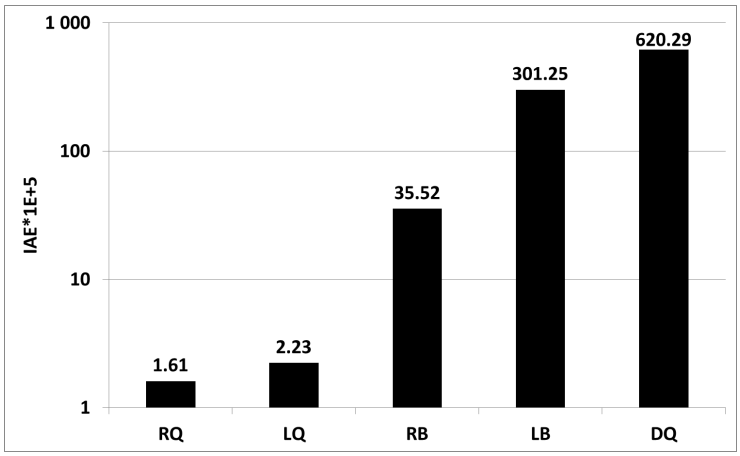


(c) RGAno

Figure B.3: Frequency Domain Indices of Ethanol–Propanol Column

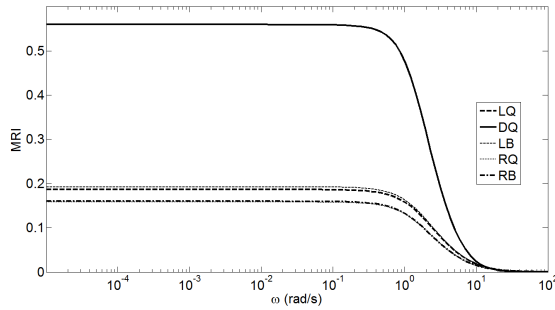


(a) flow rate disturbance

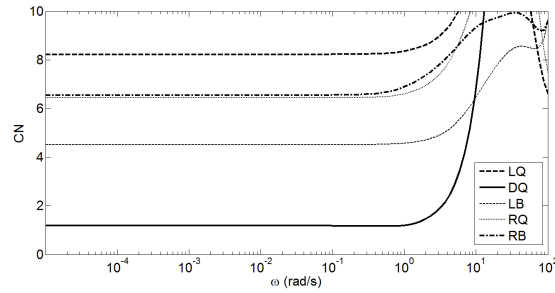


(b) composition disturbance

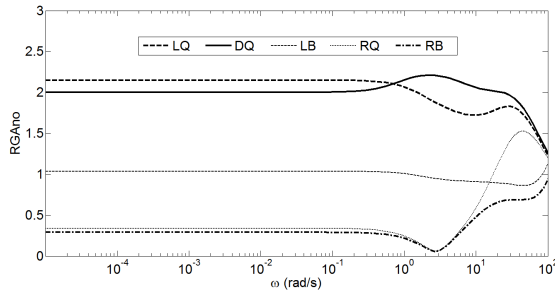
Figure B.4: IAE of Ethanol–Propanol Column



(a) MRI

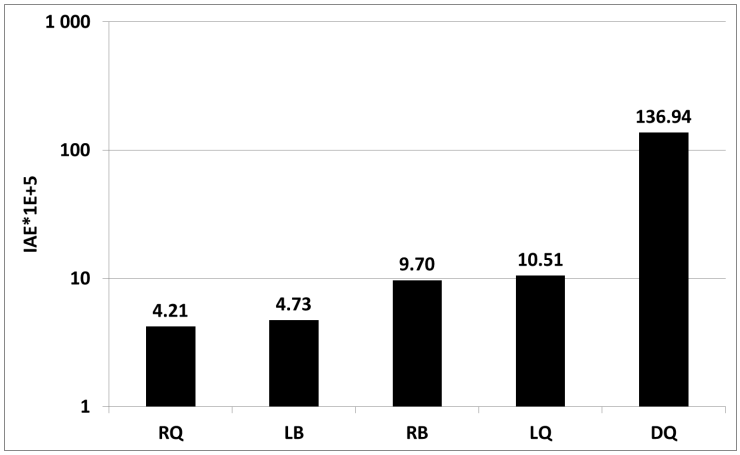


(b) CN

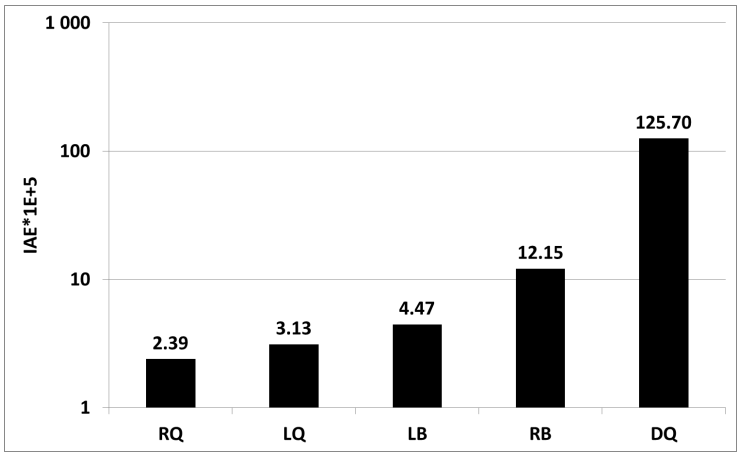


(c) RGAno

Figure B.5: Frequency Domain Indices of *n*-pentane–*n*-hexane Column



(a) flow rate disturbance



(b) composition disturbance

Figure B.6: IAE of n-pentane–n-hexane Column

Appendix C

List of Terms and Symbols

Greek letter

- Δ - difference
- η - thermodynamic efficiency [%]
- ω - frequency [rad/s]
- σ - singular value
- τ - time constant [s]

Subscript

- 0 - ambientheat reservoir
- C - condenser
- crit - critical
- irr - irreversible
- lost - lost
- ol - open loop
- R - reboiler
- sep - separation

Latin symbols

- ALK - alkane
- ARO - aromatic
- B - bottoms product
- BHI - backwards heat integrated
- CN - condition number
- CO_2e - carbon dioxide equivalent [kg/y]

- CV - controlled variable
- d - individual desirability value
- D - distillate product
- $D - fct$ - desirability function
- DS - direct sequence
- e - molar exergy[kJ/kmol]
- $\dot{E}$ - exergy flow[kW]
- EP - elevated pressure
- F - feed stream
- G - transfer function
- GHG - greenhouse gas
- GWP - global warming potential
- $\dot{H}$ - enthalpy flow[kW]
- HP - sharp syeparation, higher purity
- i - imaginary unit
- IAE - integrated absolute error
- L - reflux stream
- LP - sloppy separation, lower purity
- m - weighing factor
- MRI - Morari resiliency index
- MV - manipulated variable
- $\dot{n}$ - mole flow [kmol/s]
- $\dot{Q}$ - heat flow [kW]
- R - reflux ratio [-]

- s - molar entropy [kJ/(kmol*K)]
- $\dot{S}$ - entropy flow [kW/K]
- T - temperature [K]
- TAC - total annual cost [1000$/y]
- TSA - total site analysis
- $\dot{W}$ - work flow [kW]
- x - mole fraction [-]

Appendix D

Declarations

D.1 Declaration

I, the undersigned, Máté Haragovics hereby declare that this PhD Thesis is solely my own work and I used for its preparation only sources specified in the text. The source is clearly specified for all parts that are copied verbatim or paraphrased

Székesfehérvár, September 2014

Máté Haragovics

D.2 Nyilatkozat

Alulírott Haragovics Máté 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, egyértelműen, a forrás megadásával megjelöltem

Székesfehérvár, 2014 szeptember _____

Haragovics Máté