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Theses of the Ph.D. dissertation entitled

Complex evaluation methodology for energy-integrated distillation columns

submitted by

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Conference proceedings

1. **Hajnalka Kencse**, Máté Gábor, Péter Mizsey: Energiaintegrált desztillációs rendszerek modellezése, *Műszaki Kémiai Napok '05*, **2005**, pp 188, ISBN 9639495719, Veszprém, Hungary.
2. Máté Gábor, **Hajnalka Kencse**, Péter Mizsey.: Energiaintegrált desztilláló rendszerek vizsgálata, Műszaki Kémiai Napok '06, **2006**, pp 268 Veszprém, Hungary.
3. **Hajnalka Kencse,** Máté Gábor, Péter Mizsey: Comprehensive Investigation of Energy-Integrated Distillation, *17th International Congress of Chemical and Process Engineering*, **2006**, pp 346, ISBN 8086059456, Praha, Czech Republic.
4. **Hajnalka Kencse**, Péter Mizsey: Comprehensive Process Investigation Methodology for Energy-Integrated Distillation, *17th European Symposium on Computer Aided Process Engineering*, **2007,** pp 883, ISBN 9780444531575, Bucharest, Romania.
5. **Hajnalka Kencse**, Péter Mizsey: The Impact of Energy-Integration on carbon dioxide emissions, *Permea 2007, Membrane Science and Technology Conference of Visegrad Countries*, **2007**, pp 265, ISBN 9789639319691, Siófok, Hungary.
6. **Hajnalka Kencse**, Péter Mizsey: Investigation of Exergy Loss and CO_2e Emission for Energy-Integrated Distillation Systems, *35th International Conference of SSCHE*, **2008**, pp 49, ISBN 9788022729031, Tatranské Matliare, Slovakia.
7. **Hajnalka Kencse**, Péter Mizsey: Investigation of CO_2e Emission for Energy-Integrated Distillation Systems, INTERFACES '08 Sustainable development in petroleum refining and petrochemistry, **2008**, pp 81, 9789639319868, Sopron, Hungary.

1 INTRODUCTION

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

The chemical process design practice has developed over the years according to the requirements of the time. The aim of the process design is to find the feasible process alternatives and to choose the most suitable one for the specific production task. This process design became computer aided in the last decades which makes possible to apply more complex analysis in the early stage of design. Parallel to the design of the process further studies are needed in order to eliminate process alternatives outside the limits of the operating conditions, profitability or safety conditions. Further benefit of comprehensive process evaluation in early stage is that the late modifications with high cost can be avoided. Thus, the methodology of process design used in the past decades should be reconsidered and developed according to the criteria claimed by recent requirements. The early stage of process design was practically based on engineering design and the alternatives were evaluated merely according to their economic features. The methodology of process design should be completed with new steps. Nowadays, due to increasing energy prices and strict environmental regulations the investigation of the energy efficiency and the emissions of the process must take place simultaneously at the early stage of process design.

The primary aim of this thesis is to elaborate a complex process design methodology that evaluates the distillation systems based on exergetic, economic and greenhouse gas (GHG) emission aspects. The aim of the methodology is to determine how these three features should be applied in process design to obtain information about the accuracy of the design alternatives.

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

Retrofit design of an industrial heat-integrated distillation system is presented as case study, which separates N, N-dimethylformamid (DMF)-water mixture. The task was to examine how the capacity of the distillation based separation system could be increased by 42.8% of a distillation system consisting three columns. The performance of the existing distillation system and various increased-capacity structures have been studied using rigorous process simulation.

The secondary motivation of my work is to investigate the controllability features of the energy-integrated distillation systems and to elaborate an easy applicable controllability analysis method in order to compare energy-integrated distillation systems based on their control properties and to select the easiest controllable one. These investigation steps assure the designer that the distillation system will meet the claimed requirements.

2 LITERATURE REVIEW

The thesis studies representative distillation systems of the heat-integrated and the thermocoupling group[1]. These energy-integrated distillation systems are frequently studied in the literature, investigating their energy saving properties through comparative studies, elaborating design methods for one specific type of energy-integrated distillation sequence. Sobocan et al[2] developed a systematic synthesis of thermally integrated distillation systems. This method helps in reducing external energy input of the distillation systems by minimizing the utility

[1] Annakou, O.; Mizsey, P., Rigorous comparative study of energy-integrated distillation schemes. Industrial & Engineering Chemistry Research 1996, 35, (6), 1877-1885.

[2] Sobocan, G.; Glavic, P., A simple method for systematic synthesis of thermally integrated distillation sequences. Chemical Engineering Journal 2002, 89, (1-3), 155-172.

7 PUBLICATIONS

Papers published in scientific journals

1. **Hajnalka Kencse**, József Manczinger, Zsolt Szitkai, Péter Mizsey: Retrofit Design of an Energy Integrated Distillation System, *Periodica Polytechnic, Chemical Engineering*; 51/1, **2007**, 11-16.

2. **Hajnalka Kencse**, Péter Mizsey: Comprative Study of Energy-Integrated Distillation Systems Based on Exergy Analysis and Greenhouse Gas Emissions, *Revista de Chimie*; 60, no. 10 / **2009**, IF=0.389.

3. **Hajnalka Kencse**, Peter Mizsey: Methodology for the Design and Evaluation of Distillation Systems: Exergy Analysis, Economic Features and GHG Emissions, *AICHE Journal*, early view online, **2009**, IF=1.883

Partly related publication

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

systems investigated. The transfer matrix is subject to singular value decomposition in order to determine the frequency dependent controllability indices, which are summarized with the desirability function. I introduced and successfully applied also for the evaluation of process design alternatives (Thesis 1).

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

6 Applicability of the Results

The proposed complex evaluation methodology can be applied in the design procedure of energy-integrated distillation systems. The methodology helps to decide between the competitive design alternatives for a specific separation task.

The results of the retrofit design in Chapter 5 provide feasible scenario for the capacity increase of heat-integrated distillation systems. The results show that the heat-integrated distillation system obtained by the retrofit design has lower specific energy consumption compared to the existing heat-integrated separation system.

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

consumption and maximizing the heat exchange between the integrated columns. The proposed design method takes in account only energetic criteria.

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

The use of energy efficient distillation is beneficial also from the point of view of greenhouse gas emission since this emission is limited in most of the countries.

The emission inventory of distillation systems may contain air pollutants and residual wastes. The former is produced through the heat generation and because of the large energy demands of the distillation systems the quantity of air pollutants is significant. The quantity of the emission related to the residual wastes depends on the separated mixture. The air pollutants released by the heating system of the distillation may contain carbon-, nitrogen-, sulphur-, and halogen-containing compounds. The quality and quantity of these pollutants depend on the type of the fuel used for heating. In the case of the fossil fuels the major part of the emission is formed by the carbon dioxide (CO_2).

The chemical processes during their operation must satisfy several requirements imposed by the designers such as production specifications, operational constrains. These requirements dedicate the need for control structures, which realize the continuous monitoring of the operation. The task of the control structure usually is to suppress the influence of external disturbances, to ensure

the stability of the chemical process, and to optimize the performance of the chemical process. The works found in the literature on controllability evaluation topic do not try to aggregate the different control indices[3]. On the contrary these indices are considered individually. However, they may show opposite operability characteristics for a given control structure. Often the results of the controllability studies are difficult to interpret because of the controversial index results for a given control structure (e.g. the value of the CN is close to the desirable domain but the RGA value indicates strong interactions). In order to aggregate the different controllability indices this thesis proposes the desirability function method to optimize the multiple control characteristics problems.

3 APPLIED CALCULATION METHODS

The simulation models of the studied distillation systems are implemented in the ASPEN Plus process simulator. Moreover, the applied studies in this work e.g. exergy analysis, economic study require the use of MS-Excel connected to the process simulator where the different exergy calculating equations or the cost functions are introduced. The environmental impact assessment in the dissertation is done with the use of SimaPro software. The model developed by Gadalla et al verifies the results calculated by this software. The controllability study is carried out with the Control Design Interface of Aspen Dynamics and the results are further analysed in Matlab. The applied process simulator is used also for equipment sizing such as distillation column diameter, tray geometry, and heat exchanger dimensions.

[3] Skogestad, S.; Lundstrom, P.; Jacobsen, E. W., Selecting the Best Distillation Control Configuration. Aiche Journal 1990, 36, (5), 753-764.

Thesis 2

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

Thesis 3

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

Thesis 4

I elaborated a controllability analysis methodology, which is a simple way to evaluate different process design alternatives in order to select the easiest controllable one. The analysis is based on the state-space representation of the

These controllability indices are aggregated with the desirability function in order to simplify the decision which system is the easiest to control.

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

5 THESES

Thesis 1

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

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

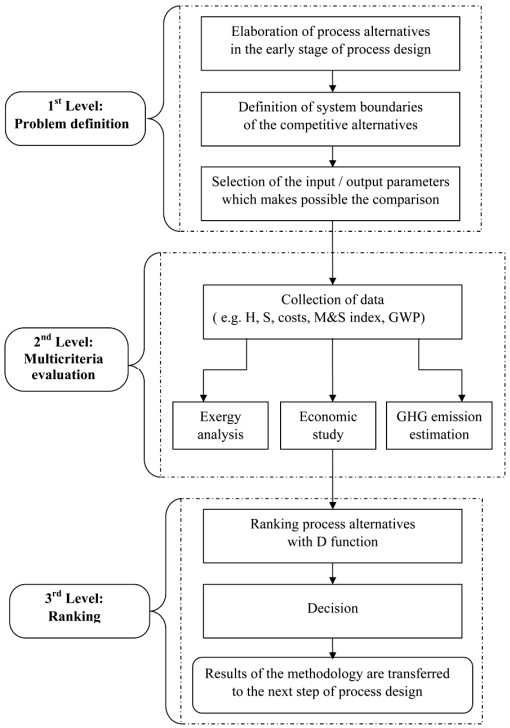
1. b.) First in this research topic, I applied the so called desirability function to rank the process alternatives. For this purpose I elaborated a summarized indicator on the basis of the desirability function to help the choice of the most adequate process alternative for the specific separation task.

4 MAJOR NEW RESULTS

4.1 Complex evaluation methodology for energy-integrated distillation columns

The thesis proposes an evaluation methodology of distillation systems that consists of three levels and takes into account exergy, economic, and emission criteria in order to find the most adequate process structure. The proposed process investigation methodology for distillation systems helps to evaluate process alternatives from a complex point of view. Following this methodology, the problem defined on the first level is suitable for the complex comparative study. The second level is the multicriteria evaluation and it forms the hearth of the methodology. On this level three different kinds of analysis are carried out in order to evaluate the distillation systems based on exergetic, economic, and environmental impact aspects. On the last level of the methodology these three aspects are aggregated by the D_{fct} in order to help the selection of the most adequate distillation design alternative giving one general characteristic figure for each process design alternative. In the case study, three energy-integrated distillation systems are investigated and compared to the conventional direct scheme. In the case of the exergy analysis the base of comparison is their thermodynamic efficiency. This analysis shows that the heat-integrated distillation structures (DQB and SQF) are the most energy-efficient among the studied ones. The thermodynamic efficiency of all the studied distillation systems is the highest when the ease of separation is symmetric, that is, the exergy loss is minimal in analogue cases. Economic study supports the results of the exergy analysis and shows that the heat-integrated distillation structures have the best economic features as well. Although the FTCDC is less economic than the other investigated heat-integrated systems but it shows energy savings compared to the conventional sequence. CO_2e emission reduction can be achieved with the use of cleaner fossil energy source, and using heat-integrated distillation schemes.

CO_2e emissions of the distillation systems can be decreased by an average 40% using DQB arrangement instead of conventional alternative.



The CO_2e emission estimation demonstrates that in most cases, the DQB has the lowest CO_2e emission but the SQF is less sensitive to product purity change. Applying the D_{fct} reveals that among the different distillation schemes, the heat-integrated DQB alternative proves to be the best applicable, since it shows the features in a wide and flexible range.

4.2 Retrofit design of an industrial heat-integrated distillation system

The thesis presents a retrofit design of an existing industrial heat-integrated distillation system consisting of three columns originally. The retrofit design case

study gave the possibility to study the heat-integration in industrial scale and to investigate the energy-integration in the case of polar mixture; therefore, this case study serves as a completion of the previous studies for hydrocarbon mixtures. The task of the work is to examine how the capacity of the separation system could be increased by 42.8% and to increase the energy saving performance. Based on the previous evaluation study the backward heat-integrated solution is investigated for the given N, N-dimethylformamid - water mixture. The performance of the existing distillation system and of various increased-capacity structures have been studied using rigorous process simulation.

The results of the study show that the capacity increase of the heat-integrated separation system from 14 tons/h to 20 tons/h is possible. The extra column that is available on-site is to be elongated by 3m, and is to be connected parallel to the existing two columns of the vacuum part of the separation system. The internals of all the columns are to be replaced by new, high efficiency Sulzer Mellapak Plus 252Y structured packings. Energy requirements of the recovery of 1kg DMF have been calculated for both the existing and for the suggested retrofit structure.

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

4.3 Operability evaluation of the energy-integrated distillation systems

I propose a simple controllability analysis that is applied on the studied distillation systems. The controllability analysis investigates the control features of the distillation systems in frequency domain and compares them based on their control properties. The controllability analysis proposed in my thesis is a simple way to evaluate different distillation systems in order to select the easiest operable one. The analysis requires the calculation of the transfer matrices of the investigated distillation systems that is subject to SVD. Based on the calculated singular values the controllability indices can be defined in the frequency domain.