BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS
Department of Chemical Engineering

Synthesis of Mass Exchange Networks Using Mathematical Programming

Ph.D. Theses

of

Zsolt Szitkai

Supervisor:

Prof. Dr. Zsolt Fonyó
member of the Hungarian
Academy of Sciences

February 2004

Introduction

The environmental impact of chemical facilities cannot be effectively mitigated by simple end-of-pipe treatments. The concept called process integration allows pollution prevention to be taken into account during the process synthesis step (e.g. Smith, 1995; Biegler et al., 1997; Mizsey and Fonyó, 1990). To the analogy of heat integration and heat exchanger network synthesis, from 1989, the concept of mass integration and mass exchanger network synthesis (MENS, El-Halwagi, 1997) have been developed.

Mass exchange networks (MENs) are parts of the separation networks of the chemical plants. The purpose of MENs is to clean the departing process streams before they are released to the sewage system or into the air. By fully exploiting the cleaning capacities of the process streams that are available on site MENs reduce both the amount of expensive external cleaning agents and the costs of the end-of–pipe waste treatment. Consequently, MENs serve direct pollution prevention goals.

With the developing algorithms (Floudas, 1995; Grossmann and Kravanja, 1997) and computer technology, from the early nineties, it became possible to routinely solve realistic process synthesis problems using mathematical programming (MP) methods. The MP-based synthesis approach (Biegler et al., 1997, Friedler et al., 1993) does not include trial and error elements, hence theoretically gives the opportunity to surpass the performance of the well established, heuristic (Douglas, 1998) or pinch (Linnhoff, 1993) design methods. The mathematical programming approach to design or synthesis consists of three major steps. The first step is the development of a superstructure (a representation of alternatives of which the optimum solution is selected). The second step is the formulation of a mathematical program. The third one is the solution of the optimisation model. These three steps are to be handled as a whole because there is a close connection among them. The solution of complex process synthesis problems using optimisation is not an easy task. The development of new optimisation algorithms and the development of better optimisation models for the various process synthesis problems are both in the scope of today's research.

At the beginning of my research, already both pinch and MP based methods existed for the synthesis of MENs. The most elaborated ones have been the following:

1. The advanced pinch method of Hallale and Fraser (1998, 2000), that can be regarded as the extension of the original pinch synthesis method of El-Halwagi (1997).
2. The simultaneous MINLP model of Papalexandri et al. (1994)
3. The insight based (though simultaneous) nonlinear programming (NLP) model of Comeaux (2000).

The pinch design method for MENS comprises two stages: targeting and design. At the targeting stage, the problem data are used in order to predict, on thermodynamic grounds, the best possible performance. The next stage is designing the network to meet the targets. The original pinch synthesis method of El-Halwagi (1997) allowed targeting only the variable costs and the minimum number of mass exchanger units (absorbers, extractors etc.) ahead of the design. Developing methods for capital cost targeting Hallale and Fraser (1998, 2000) could introduce supertargeting (i.e. targeting the total annual costs, TAC) for MENs. Deriving the optimal network structure is more or less a trial-and-error heuristic process when applying pinch methods, especially in case of large or multiple component problems. That is why MP models for MENS have been developed.

Simultaneous MP models for MENS allow the simultaneous optimisation of the structure and the operating costs without any trial-and-error conjecturing. The objective function of these optimisation models is the TAC of the MEN. The first simultaneous MINLP model for the synthesis of MENS has been the model of Papalexandri et al. (1994), which is a large, mainly nonlinear formulation. Comeaux (2000) claimed that applying pinch theory principles in generating the superstructure of his NLP model, the MEN designs of Papalexandri et al. could be improved. While reducing the complexity of the superstructure, Comeaux still suggested a strongly nonlinear MP model.

Aims of the work

The general aim of my work has been the development of new mixed integer nonlinear programming (MINLP) models for MENS and for other mass exchange applications.

At the beginning of my research there did not exist an extensive example problem based comparison that enabled rating the applicability of the previously mentioned methods for MENS. Authors of the MP models illustrated their methods with the solution of just a few example problems. The first aim of my research has been to choose the best applicable MP model from the literature and to resolve the numerous MENS example problems of Hallale (1998). It was to be expected that the MP based models would not always outperform the pinch method, since Hallale (1998) claimed that he could surpass more of Papalexandri's MEN designs. Hence it was also to be expected that the MP models would need to be extended. Papers presenting the MP models did not deal with problems like how to generate initial values for the model variables, or how to get solutions with rounded up stage numbers.

Gaining experiences from the solution of the example problems and from the comparison of the literature methods, the second aim of my work has been the development of a new MP model for the synthesis of MENs. A simple and mainly linear model was to be developed that could be integrated later into general process networks synthesis models.

The third aim of my work has been the development of MP models that allow the optimal design of industrial mass exchange applications. A hybrid distillation-pervaporation system and a stripping unit have been selected. In contrast to the MENS example problems, the industrial applications required rigorous modelling that meant a challenge during the development of the models.

Approach

My work comprised the creation and solution of MP models. MINLP optimisation problems were solved using DICOPT++ (GAMS Development Corporation, 2000), which is a standard solver available within the GAMS modelling framework (Brook et al., 1992). The GAMS program package was chosen because it is easily accesible, user friendly, and very well documentated.

Experimental data for the MP models of the industrial applications were taken from the literature. I have not carried out experiments, still, before developing the MINLP model of the distillation-pervaporation system, I visited an ethanol dehdration plant. Much useful information could be obtained from a senior engineer working there.

Major new results

1. It has been revealed that properly dealing with the removably discontinuous Kremser equation in MINLP models for MENS is a crucial point of the mathematical programming based synthesis process. A new method has been presented for handling removably discontinuous functions. The new formulation uses only one binary variable per discontinuity, hence results in simpler mathematical programs. The example problem based comparison shows that in case of large nonconvex MENS problems, the new, one binary variable method is much faster than any of the literature methods, hence enables the proper solution of larger synthesis problems. The applicability of the new formulation has been presented on a HENS problem as well. Handling of discontinuities in these special ways are necessary because currently the language of the GAMS program package does not accept conditional commands regarding the model variables.

2. Two existing simultaneous MP-based models for MENS have been compared. To achieve a better performance, the studied literature models have been extended by the proper handling of the Kremser equation. Methods for model variable initialisation and for calculation with integer stage numbers have been found. As the example-based comparison shows, the MINLP design method of Papalexandri et al., (1994) seems to be superior to the NLP design technique of Comeaux, (2000). This is not only because of the latter formulation is lacking the advantages of the MINLP techniques, but also because of the superstructure of Comeaux, (2000) is found to be too simple. The solved example problem shows that insight based supersructures constructed using the vertical mass transfer principle may not enclose the optimal structure of the MEN.

3. The extended MINLP model of Papalexandri et al. (1994) and the advanced pinch method of Hallale and Fraser (2000) have been compared by solving several example problems. Comparing the TACs of the solutions shows that the two competing approaches perform more or less equally in solving MENS problems, though

theoretically, the MP based approach should always perform better. The reason for this is revealed. It is found that the search space of the model of Papalexandri et al. (1994) is nonconvex, hence gradient based optimisation algorithms cannot find global optima for the problems. This is because of their MINLP model consists mainly of nonlinear mass balances.

4. A new, fairly linear MINLP model for the synthesis of MENs has been developed. The new model contains much less nonlinear constraints compared to models presented in the literature, and delivers simple, industrially feasible MENs in a simple computation procedure. Resulting from the linearity of the model, no special attention to the initialisation of the model variables has to be paid. Linearity of the model is achieved by assuming iso-concentration mixing in the MEN. The model is best applicable for the solution of single component MENS problems with packed columns. Extensions to multiple component problems and trayed column calculations have been presented as well.

5. A rigorous MINLP model for the design of ethanol dehydration systems consisting of a distillation column and a pervaporation unit has been developed. The model applies a rigorous, tray by tray column model, and uses experimental data for calculating the membrane transport. Using the model, optimal design and operating parameters including number of trays, feed location, reflux ratio, number of membrane sections in series, and the number of membrane modules in each section can be determined. The model gives rise to the investigation of different recycling schemes. Developing the MINLP model, several mathematical tools enabling rigorous modelling have been studied. A method for radically decreasing the number of equivalent structures covered in the superstructure is suggested and applied. A successive refinement method is developed that enables reducing the number of binary model variables.

6. Industrial scale calculations have been carried out using the new MINLP model. 12 % savings in the total annual cost can be achieved compared to an existing plant by applying 32 % additional membrane surface, by a radical decrease of the reflux ratio

(3.3 to 1.4) of the column, and by producing less concentrated alcohol in the distillate. According to the sensitivity analysis, the replacement cost of the membranes does not significantly influence the parameters of the system. Permeate recycling schemes have been studied. In all the realistic cases, total recycling of the permeate flow proved to be optimal. On the other hand, partial recycling results in slightly cheaper designs in case of low alcohol yields and radically cheaper membranes.

7. An MINLP model for determining the minimum number of theoretical stages of a wastewater stripper has been developed. A rigorous tray by tray calculation method has been employed with exact enthalpy and VLE calculations. The model has been successfully applied to the solution of an incompatible multiple contaminant industrial problem, where volatile organic compounds had to be removed from the sewage of a chemical plant.

Significance of the new results

In the framework of this dissertation I developed new mathematical programming models for the optimal design of mass exchange networks and for other mass exchange applications. The new models allow the improvement of previous designs and can be applied whereever the removal of pollutants is necessary. Applying my results in the fine chemical or petrochemical industries, pollution as well as the investment and operating costs of the corresponding technologies can be significantly reduced.

References

Biegler, L.T., Grossmann, I.E. and Westerberg, A.W. (1997). Systematic Methods of Chemical Process Design. Prentice Hall, International Series in the Physical and Chemical Engineering Sciences.

Brook, A., Kendrick, D., Maereus, A. (1992). GAMS A User's Guide. Release 2.25, Scientific Press, Palo Alto.

Comeaux, R.G. (2000). Synthesis of MENs With Minimum Total Cost. MSc thesis, Dept.of Process Integration, UMIST, Manchester, England.

Douglas, J.M. (1988). Conceptual Design of Chemical Processes. McGraw Hill, NewYork

El-Halwagi, M.M. (1997). Pollution Prevention Through Process Integration. Academic Press, 525 B Street, Suite 1900, San Diego, California 92101-4495, USA.

Floudas, C.A. (1995). Non-linear and Mixed-Integer Optimisation: Fundamentals and Applications. Oxford University Press, New York.

Friedler, F., K. Tarjan, Y. W. Huang, and L. T. Fan (1993) Graph-theoretic approach to process synthesis: polynomial algorithm for maximal structure generation. *Computers Chem. Engng.*, **17**, 929-942

GAMS Development Corporation (2000). GAMS The Solver Manuals, 1217 Potomac Street Washington, DC 20007, USA.

Grossmann, I.E. and Kravanja, Z. (1997). Mixed-integer Nonlinear Programming: A Survey of Algorithms and Applications, The IMA Volumes in Mathematics and its Applications, Vol.93, Large-Scale Optimization with Applications. Part II: Optimal Design and Control (eds, Biegler, Coleman, Conn, Santosa) pp.73-100, Springer Verlag.

Hallale, N. (1998). Capital Cost Targets for the Optimum Synthesis of Mass Exchange Networks. PhD thesis, Dept. of Chemical Engineering, University of Cape Town, South Africa.

Hallale, N. and Fraser, D.M., **(1998)**. Capital cost targets for mass exchange networks, Part I-II., *Chem. Eng. Sci.*, **53**(2), 293-313.

Hallale, N. and Fraser, D.M., **(2000)**. Supertargeting for mass exchange networks, Part I-II., *Trans IChemE*, **78**, Part A, 202-216.

Linnhoff, B. (1993). Pinch analysis. A state-of-the-art overview. *Trans IChemE*, **71** Part A, 503-522.

Mizsey, P. and Fonyo, Z. (1990). Toward a more realistic overall process synthesis - The combined approach. *Computers. Chem. Engng.*, Vol. **14**, No. 11, 1213-1236.

Papalexandri, K.P., Pistikopoulos, E.N. and Floudas, C.A. (1994). Mass exchange networks for waste minimization. *Trans IChemE*, **72**, Part A, 279-294.

Smith, R. (1995). Chemical Process Design. McGraw Hill, International Editions.

Publications

Papers published in scientific journals

1. **Z. Szitkai**, Z. Lelkes, E. Rev, Z. Fonyo
   Handling of removable discontinuities in MINLP models for process synthesis problems, formulations of the Kremser equation
   Computers and Chemical Engineering, (**26**) pp. 1501-1516, (2002)

2. **Z. Szitkai**, A.K. Msiza, D.M. Fraser, E. Rev, Z. Lelkes, Z. Fonyo:
   Comparison of mathematical programming and pinch-based techniques for mass exchange network synthesis
   Hungarian Journal of Industrial Chemistry, (**30**), pp. 149-154, (2002)

3. **Z. Szitkai**, Z. Lelkes, E. Rev, Z. Fonyo
   Optimization of hybrid ethanol dehydration systems
   Chemical Engineering and Processing, (**41**), pp. 631-646, (2002)

4. E. Rév, M. Emtir, **Z. Szitkai**, P. Mizsey, Z. Fonyó:
   Energy savings of integrated and coupled distillation systems
   Computers and Chemical Engineering, (**25**), pp. 119-140 (2001)

5. Z. Lelkes, **Z. Szitkai**, E. Rev, Z. Fonyo:
   Rigorous MINLP model for ethanol dehydration system
   Computers and Chemical Engineering, (**24**) pp. 1331-1336, (2000)

6. N. Benko, E. Rev, **Z. Szitkai**, Z. Fonyo:
   Optimal water use and treatment allocation
   Computers and Chemical Engineering, pp. S157-S160 (1999)

7. Z.Fonyó, E.Rév, **Z.Szitkai**, M.Emtir and P.Mizsey:
   Energy savings of integrated and coupled distillation systems
   Computers and Chemical Engineering, pp. S89-S92 (1999)

Conference papers published in Elsevier proceedings

8. **Z. Szitkai**, T. Farkas, Z. Kravanja, Z. Lelkes, E. Rev and Z. Fonyo:
   A new MINLP model for mass exchange network synthesis
   European Symposium on Computer Aided Process Engineering-13,
   A.Kraslawski and I. Turunen (Editors), Elsevier Science B.V., pp. 323-328, 2003

9. Z. Lelkes, **Z. Szitkai**, T. Farkas, E. Rev, Z. Fonyo:
   Short-cut design of batch extractive distillation using MINLP
   European Symposium on Computer Aided Process Engineering-13,
   A.Kraslawski and I. Turunen (Editors), Elsevier Science B.V., pp. 203-208, 2003

10. **Z. Szitkai**, A.K. Msiza, D.M. Fraser, E. Rev, Z. Lelkes, Z. Fonyo:
    Comparison of different mathematical programming techniques
    for mass exchange network synthesis
    European Symposium on Computer Aided Process Engineering-12,
    R. J. Grievink and J. van Schijndel (Editors),
    Elsevier Science B.V., pp. 361-366, 2002

11. **Z. Szitkai**, Z. Lelkes, E. Rev, Z. Fonyo:
    Optimisation of an industrial scale ethanol dehydration plant: A case study
    European Symposium on Computer Aided Process Engineering-11,
    R. Gani and S.B. Jorgensen (Editors), Elsevier Science B.V., pp. 553-558, 2001

12. **Z. Szitkai**, Z. Lelkes, E. Rev, Z. Fonyo:
    Solution of MEN synthesis problems using MINLP:
    Formulations of the Kremser equation
    European Symposium on Computer Aided Process Engineering-11,
    R. Gani and S.B. Jorgensen (Editors), Elsevier Science B.V., pp. 1109-1114, 2001

13. **Z. Szitkai**, Z. Lelkes, E. Rev, Z. Fonyo:
    Optimisation of distillation and pervaporation system for ethanol dehydration
    European Symposium on Computer Aided Process Engineering-10,
    S.Pierucci (Editor), Elsevier Science B.V., pp. 643-648, 2000

Other conference papers

14. P. Mizsey, **Z. Szitkai** and Z. Fonyo:
    Analysis for energy integrated separations and synthesis of mass exchange networks
    CAPE Forum 2004, Challenges for East-West European Cooperation in Process Modelling, Control, Synthesis and Optimization. 13-14 February, 2004, Veszprém

15. Zsolt Szitkai
    Planung von Stoffübertragenden Netzwerken durch
    mathematische Programmierung (in German)
    Frühlingsakademie der Hanns Seidel Stiftung,
    Hotel Uni, Balatonfüred, 7. Juni 2001

16. **Z. Szitkai**, Z. Lelkes, E. Rev, Z. Fonyo:
    Rigorous MINLP model for ethanol dehydration system
    Proceedings of the CHISA 2000 conference, Prague, 27-31 August, 2000

17. Zsolt Fonyó, Zoltán Lelkes, **Zsolt Szitkai**, Endre Rév:
    Optimisation of hybrid ethanol dehydration system
    Presentation at the 2000 AIChE Annual Meeting in Los Angeles,
    Session 261, Computer Integrated Manufacturing, November 13, 2000

18. Rév Endre, Fonyó Zsolt, Benkő Norbert, **Szitkai Zsolt**:
    Vegyiüzemek vízforgalmának optimális kapcsolási rendje (in Hungarian)
    PURE konferencia, Budapest, 2000. január 28.

19. Fonyó Zsolt, Rév Endre, **Szitkai Zsolt**:
    Ipari vízháztartások optimalizálása (in Hungarian)
    DAT'99, Magyar Adatbázisforgalmazók IX. Konferenciája és Kiállítása,
    Thermal Hotel Helia, Budapest, 1999. november 8-12.

20. **Szitkai Zsolt**, Benkő Norbert, Rév Endre, Fonyó Zsolt:
    Anyagcserélő hálózatok tervezése matematikai programozással (in Hungarian)
    Műszaki Kémiai Napok, Veszprém, 1999. április 27-29.

21. M. Roos, **Z. Szitkai**, H.-J. Bart:
    Reactive Extraction of Organic Acids - Influence of Salts
    Proceedings of the CHISA '98 conference, Prague, 22-28. August, 1998