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**Environmental Conscious Design and Industrial Application of
Separation Processes**

Theses of the PhD dissertation

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1. INTRODUCTION

The protection of our environment is an actual and global problem in our time. The prevention of waste formation is a main target of the environmental protection; however, the formation of wastes cannot be always avoided in certain cases. The appropriate treatment and minimisation of wastes generated during industrial manufacturing and processing, the recycling or safe disposal of the waste materials pose a great challenge. It is the task of the recent engineer community to elaborate how the already existing industrial processes can be reconstructed, replaced or substituted that they fulfil the strict environmental regulations. On the long term, the final objective of environmental protection is the invention of “zero emission technologies”.

The fundamental biological and physicochemical techniques applied at the treatment of wastes are well-known for a long time; however, the treatment processes have to be elaborated particularly for each new application. Techniques which combine different unit operations in order to increase the overall efficiency (hybrid processes) get more and more frequently applied in the field of environmental protection. At this point, it is worth mentioning the development of the clean technologies and as a part of it, the separation technologies. This latter can also be understood if the broad spread of membrane separation processes is considered.

A particular waste treatment problem usually can be solved by several techniques. Therefore, an appropriate objective function has to be defined which helps by the selection from the numerous alternatives. The

objective function has to be defined that it enables designers to rank the alternatives both from economic and environmental viewpoints.

2. AIMS OF THE WORK

The modern management environmental problems require more and more the application of such techniques which reduce the release of pollutants to the environment. Pollution prevention strategy has to be developed according to the following priorities:

- application of “zero emission technology”;
- recycling and reuse of materials;
- treatment and disposal of the waste with the extraction of its energy content.

In my work real industrial problems are addressed with environmentally conscious process engineering according to the aspects described above.

3. LITERATURE REVIEW

According to the guiding principles of the waste management the following aspects have to be considered:

- prevention that waste arises,
- minimisation of quantity and environmental risk due to the generated wastes;
- reuse and recycling of waste materials;
- environmental friendly waste disposal.

This priority order even prescribes the relation of these aspects. Waste treatment techniques with lower priority order are only allowed if no solution with the higher priority order is realizable.

In the chemical engineering the most environmental problems are caused by the technological waste waters. The technological waste waters can be classified as (1) inlet waters (e.g. water treatment, water pre-treatment) and (2) output waters or technological waste waters or process waters. My work focuses on the process waters. The wide variety of pollutants in the process waters is typical for the chemical industry. Process waters from the chemical industry are usually not neutral they require treatment, moreover, they might contain several types of organic and inorganic pollutants. Valuable compounds have to be removed from the process waters.

In the following I review the relevant separation techniques I applied in my work.

The rectification is the most frequently applied technique for the separation of liquid mixtures. Rectification has a wide range of applications in the separation technology, thus it can effectively applied for the treatment of waste waters/process waters. If the separation of the components is not possible with conventional distillation, special distillation technique has to be selected and applied. In my work azeotropic an extractive distillation techniques are applies beside the conventional technique.

Membrane separation means the selective transport of one component of mixture through the membrane because of some driving

force. Such driving force can be the concentration or pressure difference and others. The portion of the feed solution that passes the membrane is called permeate, that does not pass is the so called retentate. The term permselectivity is used to describe the property of the membrane which results that different compounds can permeate through the membrane with different rate. This term includes the two most important properties in the separation technology: the permeability and selectivity.

I selected the pervaporation from the numerous membrane separation techniques for study and application. Pervaporation is applied on the following fields:

- separation of azeotropic mixtures;
- removal of solvent tracers from aqueous solutions;
- dewatering from organic solvents;
- separation of liquids with low relative volatility.

In many cases product purity requirements can not be achieved by pervaporation. In these cases further unit operations have to be applied. Therefore, pervaporation is commonly combined with other operations like distillation or absorption resulting in new, so called hybrid separation processes. The emerging presence of hybrid separation processes in the practice enables the complex approach of problems.

The novelty of pervaporation is shown by the fact that the professional chemical engineering software packages usually do not contain the modules and databases required to describe this unit operation. According to this, the aims of this work also includes the development of pervaporation module running in a professional chemical engineering software environment which enables the precise modelling and design of

hybrid separation technologies consisting a pervaporation step. The selected software environment is the ChemCAD software.

4. DATA AND METHODS

In my research work the discussion and resolution of the real environmental problems require the study and analysis of several separation techniques. The analysis is carried out by laboratory experiments and/or computer simulations.

There are several mathematical models available which describe the pervaporation. I selected for study and application the semi-empirical solution-diffusion model. I determined the model parameters with laboratory experiments. The model parameters include the transport coefficient at a reference temperature (20°C in this case), energy of activation, and the permeability coefficient - a parameter describing the resistance of the membrane support layer. If these parameters are determined, the computer aided simulation of the pervaporation can be carried out.

During the solution of a particular problem the engineer usually can select from several alternative options. In my work I analyse all the alternatives from economic viewpoint. Based on the results of the economic analyses I select the best option. Objective function of the economic analyse is the total annual cost.

5. LABORATORY EXPERIMENTS

1.1. Waste Solvent Removal from Process Waters with Rectification (end-of-pipe treatment of waste waters)

My laboratory test results proved that the volatile organic solvents can be removed from the studied industrial waste waters; moreover, dichloromethane can be also removed from halogen-containing waste waters.

My aim was to design such rectification column in which waste waters of different composition can be treated on a similar way. I determined the operational parameters (number of trays, feed location, reflux ratio) of the column. Under the consideration of the desired capacity information I designed columns which have been already built in the industry.

I worked out a strategic plan for the treatment of fine chemical and pharmaceutical process waters. The results of my research are summarized in **thesis 1**.

1.2. Solvent recovery from waste water

I concluded from the investigation of some operating industrial separation technologies that the solvent recovery techniques can be improved from both the economic and environmental viewpoints. For the recovery of tetrahydrofuran (THF) from THF-water mixture a novel hybrid process based on pervaporation (PV) and rectification (D) including a pervaporation step is designed. It has better economic indicators. Compared to the old recovery technology, the operational costs can be

reduced to 84%, the total annual cost can be reduced to 78% with the novel solution.

The investigation of the THF-methanol-water ternary mixture shows that remarkable reduction can be achieved with the launching of the novel hybrid process. In this case, the operational costs can be reduced to 60% and the total annual cost to 90% of the old separation technology. The basis of these positive changes is the selection of the appropriate technique which is strictly connected with the significant decrease in the THF losses. Based on my research results, I recommend the use of a pervaporation steps in the above mentioned cases in order to avoid superfluous solvent losses and to guarantee low energy consumption.

It can be concluded that the investigation of separation technologies and their development is a feasible research activity. The development of the separation technologies can result both in a less polluting and a more economic alternative. Such design option is in accordance with the forth paradigm of the chemical engineering.

I summarize my results in **Thesis 2**.

1.3. Zero emission hybrid separation processes based on pervaporation

The aim of my work is to develop a pervaporation module running in the professional process engineering software environment. I selected the Rautenbach-type semi-empirical ‘solution-diffusion model’¹ as the basis of the mathematical modelling. The original model assumes isotherm conditions, however, I integrated a heat balance equation into the model

¹ Rautenbach R: Membrane Science and Pervaporation Technology Series 1; (szerkesztő: R.Y.M. Huang) Pervaporation membrane separation processes, Elsevier, New York 1991.

which enables the simulation of pervaporation also under isothermal and adiabatic conditions. Moreover, the heat balance equation enables the determination of the energy requirement of the separation, too. I summarize my results in **Thesis 3**.

In association with my results presented in Thesis 3, I perform the high accuracy analyses of hybrid separation processes including pervaporation steps. The analysis is carried out in professional chemical engineering software environment. According to a real industrial case study, I investigate several options for the real industrial separation task in order to find the optimal configuration. The solution options include consecutively connected distillation and pervaporation processes. I consider even isothermal as well as adiabatic pervaporation. adiabatic pervaporation in my analysis. The optimisation is carried out with dynamic programming considering an ethanol-water as inflow mixture. I also compare the new hybrid processes with a classic azeotropic distillation. The total annual cost is selected as objective function. I summarize my results in **Thesis 4**.

6. MAJOR NEW RESULTS

Thesis 1

I performed the design of new rectification processes for the removal of volatile organic and organic-halogen content from fine and pharmaceutical process waters. These processes make possible the significant reduction of the COD and AOX contents of the process waters, in several cases even under the draining limit values.

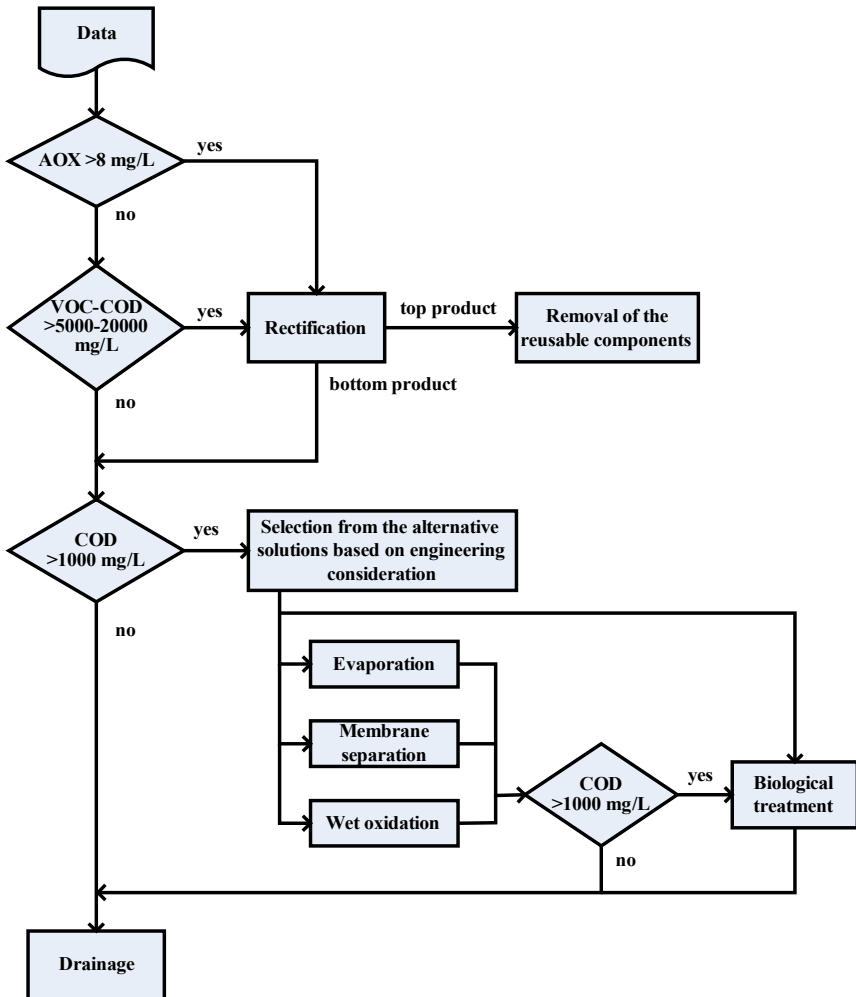
I developed a strategy for the complex treatment of fine chemical industrial and pharmaceutical waste waters. The strategy includes the sequence of application of the different physicochemical and biological treatment options [1, 5].

Thesis 2

I worked out new solvent recovery processes for tetrahydrofuran (THF) recovery. The basis of the process are provided by industrial case studies. The central point of the processes is that pervaporation is combined with different kinds of distillation (classical and azeotropic) techniques. The new hybrid processes obtained do not use new, extra material addition and the THF loss can be decreased with several orders of magnitude [2].

Thesis 3

I improved and developed the Rautenbach-model for the modelling of pervaporation. The key points of the development is that I considered the heat balance in the model and I enabled the model so that it became possible to apply the model in professional simulator.



Strategy for the treatment of process waters

The model can be used for the rigorous modelling of both isothermal and adiabatic pervaporation in professional flowsheeting software environment [3, 4].

Thesis 4

I determined the optimal hybrid separation structure for the separation of azeotropic mixture. The optimisation was carried out with dynamic programming. The investigated industrial mixture was the ethanol-water one based on industrial example. The hybrid separation structure consists of pervaporation and distillation that I connected in different sequences. As the result of the optimisation I determined that the optimal structure that is the distillation followed by pervaporation.

If extra pure ethanol should be produced (higher than 99.7mass%) than the optimal structure is the distillation, pervaporation, distillation sequence. I determined the optimal parameters for both isothermal and adiabatic pervaporation (equipment sizes, flows, compositions) [3].

7. PRACTICAL APPLICATION OF THE RESULTS

The two distillation columns I designed for the cleaning of technological waste waters (process waters) from COD and AOX were completed in the pharmaceutical industry and they operate according to my plans.

The new elaborated distillation process for the separation of tetrahydrofuran-methanol-water is applied in the industry.

The process designed for the separation of the THF-water system is ready for industrial application.

The ChemCAD firm accepted the pervaporation model I developed with improvement of the Rautenbach-model and integrated in its software package. This enables the rigorous modelling of the pervaporation together with other unit operations. This feature is applied in my work during the optimisation task related to the industrial case study (ethanol-water).

8. LIST OF PUBLICATIONS

Publications in close relation with the thesis work

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3. **Katalin Koczka**, Peter Mizsey and Zsolt Fonyo: Rigorous modelling and optimization of hybrid separation processes based on pervaporation, *Central European Journal of Chemistry*, **2007**. 5, 1124-1147 (IF:0,754, I:1).
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5. **K. Koczka**, and P. Mizsey: New area for Distillation: Wastewater treatment, *Process safety and environmental protection*, **submitted to journal**.

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7. **Katalin Koczka**, Péter Mizsey, Zsolt Fonyó: Analysis and optimization of hybrid separation systems based on pervaporation, *Periodica Polytechnica* **2007**, 51/2 pp 93.
8. **K. Koczka**, P. Mizsey, Z. Fonyo: Development and Analysis of Hibrid Separation Systems Based on Pervaporation, *ISIE 2005 Conference 2005*. júni 12-15 Stockholm, Sweeden pp 101-102.
9. **Koczka K.**, Mizsey P., Manczinger J., Deák A., Rezessy G., Fonyó Zs.: Új hibrid eljárás tervezése tetrahidrofurán regenerálására, *XII. Membrántechnikai Konferencia*, Budapest, 2004. szeptember 02. pp 33-35.
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11. **Koczka Katalin**, Deák András, Szanyi Ágnes, Manczinger József, Rezessy Gábor, Mizsey Péter, Fonyó Zsolt: Pervaporáció vizsgálata alkohol-víz elegyek elválasztásánál, *AWARENET, Szimpózium az agrár-és élelmiszeripari hulladékok csökkentésének lehetőségeiről*, Budapest, **2003** október 29. pp 40-43.

Oral lectures:

12. **Koczka Katalin**: Pervaporáción alapuló hibrid elválasztási műveletek optimalizálása, *Műszaki Kémiai Napok '07, MTA Műszaki Kémiai Komplex Bizottság és MTA Műveleti Munkabizottság ülése*, Veszprém **2007**. április 27.
13. **Koczka Katalin**: Új hibrid eljárás tervezése tetrahidrofurán regenerálására, *Doktornáns Konferencia*, Budapest, **2007**. február.
14. **Koczka Katalin**: Pervaporáción alapuló hibrid elválasztási eljárások analízise és optimalizálása, *Doktornáns Konferencia*, Budapest, **2006**. január.

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25. Jalel Labidi, Zsolt Szitkai, **Katalin Koczka**, Rodrigo Llano-Ponte, Peter Mizsey: Heat Exchangers Network Synthesis for Pulp and Paper Processes Using Different Methodologies, *International Mediterranean Modeling Multiconference 2006*. October 4-6. Barcelona, Spain. Angol nyelvű előadás
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