1. Study of off-cut recycling strategies for separating multicomponent azeotropic mixtures by the traditional batch rectification (BD), batch extractive distillation (BED) and batch heteroazeotropic distillation (BHD). Study of strategies not investigated before and optimization of these strategies.

a. We studied the effects of off-cut and entrainer recycle on the *batch extractive distillation* (BED) of two mixtures: (1) acetone (A)-methanol(B) with water(entrainer,E), and (2) isopropanol(IPA,A)-water(B) with dimethyl-sulfoxide (DMSO,E). We considered three-batch processes. For Mixture 1, we concluded that the B content of the recycled E must be low to avoid adverse effects. For Mixture 2, the process was not sensitive to the B content of E. For both mixtures, off-cut recycle was very favourable for the recovery, but it decreased the capacity. At the same time, the consumption of fresh E decreased.
We have also optimized the above processes using a genetic algorithm (GA) coupled to the flow-sheet simulator ChemCAD. The objective function was the profit of the individual batches. The results showed considerable improvement in the profit, as well as an increase of the capacity. The optimization highlighted the economic importance of recycling the expensive entrainer (DMSO).
b. We have also studied the off-cut and entrainer recycle for *batch heteroazeotropic distillation (BHD)*. IPA(A) was dehydrated using toluene (E). First, we investigated several operational strategies of BHD for a single batch then three-batch processes. Mode I (sequential distillation and decantation) was infeasible, while by Mode II (simultaneous distillation and decantation), recovery of A increased and the E consumption decreased.
Optimization with GA approaching the global optimum was very time-consuming, therefore, we tested a faster method (downhill simplex algorithm of Spendley) for the optimization of a BD and BED process. This method could not approach the global optimum, although it significantly improved the value of objective function in a shorter time.
Later, the above three-batch process was optimised by maximising the profit of the individual batches with a GA. For Mode I by optimisation the profit greatly increased, for Mode II the increase was moderate as it was already high. However, recycling decreased the E consumption of the optimised Mode II process to less than its half.
c. *Dehydration* of an industrial waste solvent mixture containing methyl ethyl ketone(A), IPA(B), water(C) and toluene(D) *by BHD* was also studied. B was recovered by using toluene as E. The results of conventional BD were compared with those of different operational policies of Mode II of BHD: Strategy A, B and a new strategy (combination of Strategies A and B) giving high recovery while increasing significantly the production speed.
We studied the possibility of using cyclohexane instead of toluene as E. The results of conventional BD were compared with those of different operational policies of Mode II of BHD: Strategy A, B and combination of Strategies A and B. We also compared the results with those of BED using DMSO as E. Cyclohexane proved to be slightly worse considering the recovery of IPA, but it provided significantly higher production speed than toluene. BED proved to be the worst policy considering both the production speed and the recovery.
d. In collaboration with French and Chinese researchers we published an extensive *review paper on extractive distillation*. The papers on BED and its optimization were reviewed, as well.

e. We investigated to what extent and how the processing capacity can be increased by applying a second, smaller column as pre-fractionator for a larger BD column.

e.1. We studied an industrial waste solvent regeneration process performed by *two BD columns of different size*. The aim: to recover acetone (B) from an aqueous mixture containing small amounts of dichloromethane (A). In much smaller Column I fore-cut and main-cut are taken. The latter is further distilled in the larger Column II, where fore-cut and main-cut are taken, as well. Main-cut of Column II is the product B. The optimisation of the specific energy demand (SED) of the process was performed by a GA coupled with ChemCad for five different compositions. The compositions studied were the average one (Case A_0C_0) and the four possible combinations of the minimal (-) and maximal (+) A and C (water) concentrations. The optimisation variables were the stopping criteria and the reflux ratios of the steps. SED was the lowest for A_-C_+ and the highest for A_+C_- concentrations. For A_-C_+ in Column II the fore-cut withdrawal could be omitted.

When only Column II was used for the separation, SED was lower than for the two-column system. However, with the two-column system higher amount of waste solvent can be processed. The two-column system can be better considering the environmental impact, when a given quantity of waste solvent must be processed in a given time because the waste not processed must be incinerated.

On the optimization results linear response surfaces were also fitted. We proved that it is possible to predict SED of the process by the previously fitted response surfaces. Operation of the two columns in parallel was infeasible since in Column I the purity requirements were not fulfilled. We studied two different options of recycling the still residues to decrease the loss of B: re-distillation in Column II and mixing to the fresh feed in Column I. We evaluated all the calculations from economic and environmental points of view, as well, by calculating the weekly profit and the environmental impacts (with WAR algorithm). The two-column process was better than the single-column one both from economic and environmental point of view when the still residues were recycled for re-distillation in Column II.

e.2. The application of a second, smaller BD column to increase the processing capacity was studied with two case studies: recovery of acetone (AN) and acetic acid (AA) from their aqueous mixtures. Three different compositions were studied with 20, 50 and 80 mass% of organic component. In the case of AN, the distillate, whilst in the case of AA, the still residue of several batches of Column I was further distilled in Column II. The processing capacity of the two-column process was maximised using a GA. The optimisation variables were the reflux ratios of the two columns and the stopping criterion for Column I. The recovery of the organic component obtained by the single-column process was specified as a constraint for the two-column process giving higher capacity than the single-column one for higher concentrations of the more volatile component (for 50 and 80% AN, and for 20% AA). We also found that at the maximal capacity of the two-column process, the operation times of the two columns are equal if the distillate, but not if the still residue of Column I is treated in Column II.

e.3. We also studied if general conclusions can be drawn for the processing capacity increase. Assuming constant relative volatility we developed a simplified model for quickly simulating both the single- and two-column processes. The relationship between processing capacity, product purity and recovery specifications, feed composition and numbers of trays was derived. We studied the influence of all parameters on the distillation times for both processes. The

conclusions obtained with the simplified model were validated by rigorous simulations for the n-heptane/n-octane separation.

f. We used the Nelder-Mead simplex and the Box complex derivative-free methods to optimize a batch distillation process recovering methanol from a five-component waste solvent mixture, which we previously optimized using a GA. The optimization was performed by an optimization program written in Excel in VBA coupled to the Chemcad flow-sheet simulator. We investigated the effect of the parameters of the simplex, complex and GA on the value of the objective function (profit) and the number of simulations required. The best objective function value was obtained by the simplex method. Both the simplex and the complex generally gave higher values than the GA but required only one fifth as many simulations on average, which considerably accelerated the optimization. The computational effort of the simplex was generally lower than that of the complex, but the median objective function value of the latter was higher. Thus, the calculations demonstrated that simplex and complex methods can be successfully applied to make the optimization of batch distillation processes faster.

2. Optimization of the semi-continuous distillation by varying the location of feeding

Different batch and semi-continuous (semi-batch) distillation (SBD) operational policies were studied by dynamic simulation with a professional flow-sheet simulator, and compared on the basis of the specific energy demand. The traditional way of SBD is to feed one part of the charge continuously into the reboiler of the batch column (SBD1). In the first case study, the less volatile component (morpholine, B) had to be produced from a dilute aqueous solution in high purity.

We suggested new operational policies, which were tested for another mixture (acetone-water), as well.

We have studied a new binary mixture (dichloromethane-acetone) where the optimal feed plate of continuous distillation was higher in the column. The influence of the feed composition was also studied on the energy demand of the different operational policies. We also proposed two new policies for SBD2 where the feed plate is fixed. In the first one, a batch distillation step is applied after an SBD2 step. In the second one, SBD2 is divided into two steps with different reflux ratios. With both new operational policies, the energy demand was significantly reduced. The best operating policy was the two-step SBD2.

We extended the application of SBD to the separation of a ternary mixture (n-hexane(A), n-heptane(B), n-octane(C)). We have investigated BD, SBD1 and SBD2 policies with both direct (A is obtained in the first step) and indirect sequences (C is obtained in the first step). SBD2 policy in indirect sequence had the lowest energy demand compared to all other batch and semi-batch policies.

3. Investigation of the facilities (e.g. heat integration, dividing wall column (DWC)) for reducing the energy consumption of distillation columns by optimising these systems. The separation of the low relative volatility and azeotropic mixtures is also studied.

Different vapour recompression (VRC) and bottom flash processes were investigated and compared for a well-known industrial separation problem (C4 split) by rigorous simulation. For a wide range of feed composition, the effects of the main operational parameters of the heat pump system were studied and the relevant operational parameters were optimized to minimise the compressor power and thus the pay-back period. By recycling or by-passing the working

fluid (depending on the process and on the feed composition), significant reduction was reached in the motor power and the pay-back period.

We have studied the separation of a maximum-boiling azeotropic mixture (water-ethylenediamine) by a pressure-swing distillation process (PSD) first at fixed column pressures. The total annualised cost (TAC) of the process is minimised, in a first step, by a genetic algorithm coupled to the flowsheet simulator. In a second step, different options to reduce the energy demand have been investigated, such as applying partial heat integration (PHI) or vapour recompression heat pumps (VRC). Heat pumps are applied either for only one or both columns with the possibility of recycling or by-passing the working fluid. PHI had the lowest TAC and by studying the influence of steam and electricity prices, we proved that it is the most economical configuration in a wide range of price combinations. The environmental evaluation of the different processes was also performed by calculating CO2 emissions and Eco-indicator 99 values. Heat pump-assisted processes had lower values compared to the other ones, especially with optimal working fluid flow rate. PHI or FHI leads to a reduction of both above indicators, but they are still higher than those of heat pump-assisted processes.

Later, the pressure of the high-pressure column (P_{HPC}) was also included in optimisation variables. The optimum of P_{HPC} was around 4.5 bar (instead of the original 2.0 bar) for all processes. The TAC decreased around 30% due to the optimisation of P_{HPC}.

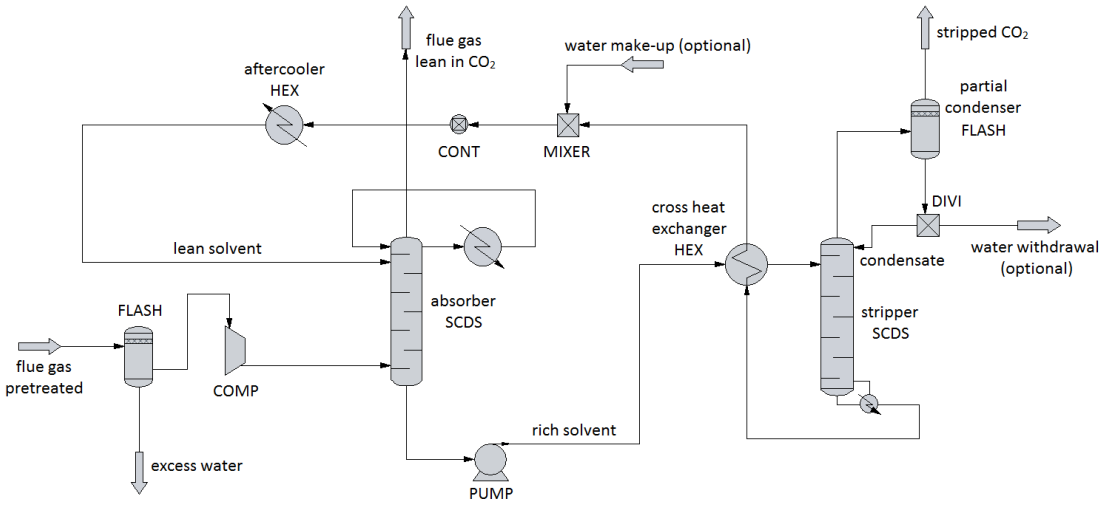
4. Study of the separation processes of the bioethanol production (concentration and dehydration) by computer simulation to reduce the energy demand. Investigation of the facilities for energy integration.

The heat integration possibilities for the reduction of external energy demand of a bioethanol plant were investigated. The case study was based on data from an operating demonstration plant producing second-generation solvent-free bioethanol. The product is a value-added chemical instead of fuel and its production does not compete with food production for raw material. We studied the heat integration of different streams and distillation columns using the pinch methodology and proposed three different variants with energy savings between 17-54%. By the additional application of a heat pump, the heating demand could be further reduced, but at the cost of consumption of electrical energy.

The heat integration possibilities were also studied for a modified process where the pressure of the last distillation column is higher than the atmospheric one. In this case heat integration possibilities generally gave higher energy savings but resulted in more complicated heat exchanger networks. The compressor duty of the heat pump was also higher.

We performed the economic evaluation of the configurations proposed by calculating TAC. Because of the high cost of the compressor, the application of a heat pump was not economical. The lowest TAC was reached by the heat integration of all streams and the reboiler and the condenser of the first and third column, respectively. However, the TAC of heat integrating the above-mentioned reboiler and condenser alone is only slightly higher. Additionally, we have studied the influence of the concentrations of the most important organic impurities in the feed and applied multi-stage compressors instead of the single-stage ones to avoid the excessive temperature increase of the working fluid.

5. Study of the post-combustion capture of carbon dioxide by reactive absorption with simulation (in collaboration with the Department of Energy Engineering of BME). Comparison of different absorbents. Study and optimisation of different configurations for the reduction of the energy demand of the process.
Reduction by 85 % of the CO_2 emission of a coal-fired power plant by three different aqueous amine (MEA, DEA, MDEA) solutions was studied by simulation with the ChemCad professional flow-sheet simulator. The influence of the most important operational parameters of the absorber and stripper columns on the energy demand of desorption was studied first in open (without recycling the lean solvent and wash water), then in closed loop (see figure).
Their optimal values resulting in the minimal desorption energy were determined. In the absorber, the decrease of temperature of the lean solvent had considerably favourable effect only for DEA and MDEA. For MEA the mass flow rate of solvent is less than half of that of the other two amines. The (slight) increase of the pressure of the stripper made the reduction of the heat duty of reboiler possible by better exploitation of the cross-heat exchanger. The lowest specific energy demands of desorption (MW/kg CO_2): MEA: 2.82, DEA: 2.58, MDEA: 2.67. However, the heat duty of the cross-heat exchanger and the total cooling energy demand are much lower for MEA than for the other solvents.
The reduction of the CO_2 emission of a coal fired power plant by aqueous NH_3 solutions was studied by simulation in a diploma work, already using the ASPEN Plus flow-sheet simulator.



General closed loop ChemCad model of the system

6. Introduction of the results of the research works and application of the computer programs and laboratory distillation devices purchased within the framework of the project for the development of the education (Modelling of Processes and Equipment, Diffusion Processes and Equipment, Individual Projects, Diploma Work A&B etc.).
The ChemCad professional flow-sheet simulator whose yearly maintenance fee was covered from the budget of the project was applied for educational purposes in several subjects (Simulation of Processes of Chemical and Food Industries (BSc), Modelling of Processes and Equipment (MSc), Individual project, BSc project work, Diploma work).

The costs of maintenance and further development of the laboratory batch distillation column and equipment used also for educational purposes were covered from the budget of the project. Several BSc project, diploma theses and 1-2 "TDK" work were written on the topics of the project every year.

Further results:

a. The senior researcher of the project Gabor Modla successfully defended his DSc thesis in autumn of 2016.

b. The young researcher Laszlo Hegely won Bolyai scholarship in 2020 and Bolyai + in 2021.

c The PhD student of the leading researcher Mr. Laszlo Czetany successfully defended his thesis in the field of Hydrodynamics and Building Service Engineering.

d. Participation at international conferences from the resources of OTKA:

Hegely: 2017: CIFQ-2017 Saint-Lô (France, session chair), ESCAPE-27 Barcelona,
2018: ESCAPE-28 Graz, D&A2018 Florence, 2019: PRES'19 Agios Nikolaos, Crete, 2020: PRES'20 Xi'an (China, on-line)

Lang: PRES'17 Tienjan (session chair), D&A2018 (member of the scientific committee), PRES'19 (session chair), PRES'20 (keynote lecture).

e. Reviewing during the 5 years of the project:

Articles of journals with IF: Lang: 50, Hegely: 55

PhD thesis (from the Indian Institute of Technology Karaghpur): Péter Láng

D&A2018 conference papers (Lang: 4, Hegely: 4, Denes: 1)

f. Bence NEMETH, who intends to obtain PhD from the industry, was working very successfully in solving the research tasks of the project. He was the first author of two D1 and one Q2 articles and a 10-page conference paper.

g. Two PhD students begun their studies with the Scholarship Hungaricum at the research group (in 2019 and 2021. respectively). Ms. Mariem Ferchichi (from Tunesia) passed successfully on the complex exam in 2021, but the continuation of her PhD work is doubtful because of her familial and financial difficulties which are in connection with the COVID.

h. In 2017, by using the resources of OTKA (for his cheap plane ticket and moderate accommodation costs), we invited and hosted Ass. Prof. Jana from Indian University of Technology of Kharagpur, who is a well-known researcher and delivered a seminar.

Obstacles

We were able to realise the purchase of the PC and of the notebook only with one year delay. We were able to begin to use the software ASPEN Plus with one year delay.

The best Hungarian MSc students do not remain at BME as PhD students, but they go to the industry for a much higher income. Dr. Denes, researcher in the project, has left the BME because of his low salary. The senior researcher Dr. Modla could not participate in the second half of the project because of his increased duties in the Sanofi-Chinoin. Therefore, we asked permission to finish the project with one year later (at the end of the 4th year).

Because of the COVID'19 the working conditions of the research became more difficult. Therefore, we asked the prolongation of the project finally until the end of the 5th year.

Though the financial resources of the project were totally consumed by the end of the 4th year we successfully continued the research in the field of the project.