FINAL REPORT OF OTKA 112699

„CAPTURE OF CO_2 FROM BIOGASES AND INDUSTRIAL FLUE GASES”

DURATION TIME: 2015-2019

In these project 86 publications were written plus conference presentations, proceeding, open access publication in Hungarian and English in our journal (http://www.ceep.envproceng.eu/), approx. 150 pieces more were delivered. Four "summa cum laude" PhD works/theses were defended in the topics of the project.

The total impact factor of the 86 publications is relatively high in our research field (technical chemistry) **162.259**

We have won different awards such as the „Pro Progressio, Innovation Award” and especially the "Gran Prize" awarded by the Swedish Chamber of Commerce and the "Highly commended" award from IChemE (United Kingdom). (Other awards are listed in our home page, see http://www.envproceng.eu/)

We actively participate in the work of the „Environmental CO_2 Partnership” (http://eco2p.eu/) founded by University of Miskolc and prominent industrial partners.

1.) Carbon capture

1.1 Model definition

Since the most frequent process being used for post-combustion capture system is an absorber-desorber system, we studied such a system (Figure 1) where the absorbent 30wt% aqueous monoethanolamine solution was.

There are different absorbents[1] according to the aim of the carbon capture. MEA belongs to the most reactive group and its special features enable appropriate, almost total carbon-dioxide removal.

For the sake of the determination of the adequate thermodynamic method measurements were taken to verify the different modelling results. On the basis of the experiments we determined that the e-NRTL thermodynamic model is adequate for the modelling. We added our own data, too.

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[1] https://www.newpointgas.com/services/amine-treating-plants/

The modelling activities were carried out with ASPEN professional flowsheeting simulator.

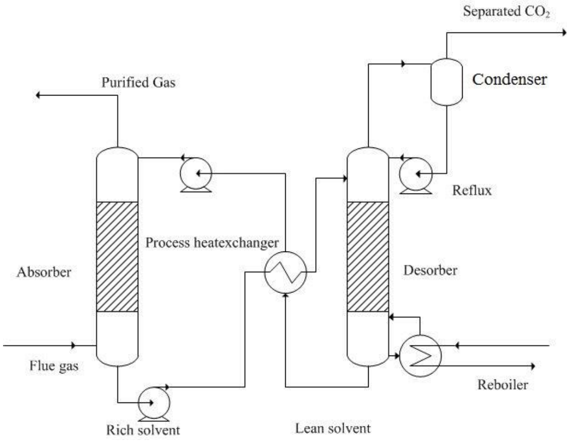

Figure 1, CO_2 capture system

In the following the building and evaluation of the absorber-desorber process model by comparing results with experimental data.

The model is evaluated in different levels. Starting with the thermodynamic model, as discussed before, the heat of absorption is calculated and compared based on different literature data and built in software methods. Many of the results turned out to be equally good since the results of literature data are scattering in a wide range. A pattern is observed that the heat of absorption in the absorption desorption range is proportional to the temperature in Kelvin. Investigating the mass transfer model, the classic equilibrium and non-equilibrium model approach is evaluated. The process model is then compared with pilot plant experiment results. By focusing on certain parameters that characterize the operation the best, the non-equilibrium model is superior to the equilibrium model. Based on the results of column temperature and concentration profiles, regeneration energy demand the simulation results are within 10% to the experimental runs for two different CO_2 content of test gases. Different types of flue gases including test gases and biogas are applied to the evaluated model in order to investigate the change of the optimal operating conditions. This investigation is carried out for constant gas flow and for constant boiler output. It is shown how the CO_2 content, absorbed amount of CO_2 and specific desorption energy demand are in a function of each other.

As a conclusion, it can be concluded that the e-NRTL model and the “rate based” column algorithm deliver appropriate results.

The equilibrium column model is not adequate for this modelling problem. If this model is used, the absorber completes its task, according to the modelling results, in one equilibrium stage. But in the pilot plant absorber column there are more than one units if the HETP value is studied. That means, in this absorption problem, which is a reversible chemisorption problem in the reality, only the rate based column model may be used since it does not assume equilibrium between the compositions of the streams leaving the modelling section. On the other hand, the simulated data, when rate based model is applied, are in agreement with the pilot plant measured data presenting that for such systems only the rate based model should be applied.

Different investigations were completed:

The constant gas flow and the constant boiler output investigation is extended with a so called flexibility analysis where the removal rate is varied. The CO_2 balance of the capture process is investigated in various CO_2 removal rates assuming different cases. Finally the capacity and efficiency improvement of such process is studied. Different cases are studied and then compared with each other. These cases are boosting the reboiler energy, varying the desorber pressure, inserting second absorber-desorber system and increasing the absorber column height. Results show that the specific reboiler energy demand can be kept reasonably low, well above 90% CO_2 removal rate with reasonably high desorption pressure and high absorber columns. In case of retrofitting an existing capture system a second series of absorber-desorber system can keep the specific reboiler energy at reasonable levels while increasing the overall capture capacity.

1.2 Use of different energy sources for efficient carbon capture

CO_2 is the primary greenhouse gas (GHG) due to its large quantity of anthropogenic emission. In this work the amine based carbon capture process and the CO_2 storage, called Carbon Capture and Storage (CCS) is analyzed from different viewpoints. PESTLE (Political, Economic, Social, Technological, Legal and Environmental) analysis of the CCS alternatives (Fossil based, improved process, Renewable based) is investigated in detail and the alternatives are also compared with the uncontrolled CO_2 release using Life Cycle Assessment (LCA) methods. Life cycle inventory data is set up and analyzed with four life cycle impact assessment methods. In order to conclude the comparison of CCS and the uncontrolled release of CO_2 a Multi-Criteria Decision Analysis (MCDA) is also applied with Multi Attribute Value Theory (MAVT) method. Our results show that applying process improvement and renewable energy sources (e.g., biogas) for absorbent regeneration result in a CCS technology of much smaller environmental and social impacts, and therefore the CCS technology becomes more favorable than the uncontrolled release.

1.3 Electrochemical conversion of the captured CO_2 to methanol in MEA absorbent

There are electrochemical methods to turn molecules into another one. In our project electrochemical methods were applied to transform CO_2 into another molecule.

The idea that this transformation should be carried out in the absorbent, that is, in 30wt% aqueous monethanolamin solution. At special voltage the transformation takes place and with gas chromatograph methanol was detected.

This successful experiments open up new horizon for the carbon capture.

1.4 Carbon-dioxide capture of geothermal origin, a practical case study

If geothermal water is taken there is always solved gas in the water. If the water is taken, at atmospheric pressure the dissolved gas goes into the atmosphere.

The dissolved gas 96% CO_2 and its task was to capture this gas at low temperature so that waste heat can be used for the operation.

We designed the appropriate system but it will be completed if the use of captured CO2 has been already solved.

Industrial secrecy prohibits us the detailed description.

2.) Low emission separation techniques

2.1 Removal of organic halids from process wastewater

The organic halogens/halids are crucial in the case of any wastewater treatment alternative.

In the fine chemical industry it is especially true since there are process wastewaters (PWWs) and used solvents which are inevitably arising during the technology. On the other hand, these PWWs contain valuable organic compounds that can be utilized e.g. solvents of another industrial process. Economical methods are recommended for practical use, which can reduce the disposal ratio of the process wastewaters with higher values of chemical oxygen demand or total organic demand (COD, TOD) and adsorbable organically bound halogens (AOX) than the corresponding emission limits. To complete this goal special techniques are to be applied the so called physicochemical treatment methods. Such treatment alternatives are also the part of environmental sustainability.

In the engineering practice there are two basic alternatives of physicochemical treatment for the removal of volatile compounds and AOX from PWWs: stripping with air or stripping with steam. These alternatives were investigated and compared in the case of a real industrial problem. The two alternatives were modelled in the professional software environment of ASPEN Plus®. It is proved that the steam stripping shows better operability and economic performances than the air stripping moreover the volatile and/or AOX compounds can be recovered in the distillate and they can be reused improving the sustainability.

On the basis of modelling and experiments we designed a rectification column for EGIS Pharmaceutical that has been operating better than the expectations. Figure 2 shows the rectification column of our design.

Our method and design (Figure 2) were awarded.

Figure 2, AOX removal column at EGIS Pharmaceutical

2.2 The combination of organo- and hydrophilic pervaporations opens up new horizons for membrane unit operations

The work is motivated by an industrial separation problem, that is, isobutanol removal from aqueous mixture. To complete this goal a hybrid separation system of organophilic–hydrophilic pervaporation system is designed applying Sulzer PERVAP™ 4060 and 1510 membranes and investigated to obtain information about the separation of isobutanol–water mixture. The aim of research is to rigorously model and optimize this novel hybrid process. Permeation fluxes, permeances, selectivity and separation factors are experimentally determined for this hybrid system. The pervaporation separation index (PSI) and selectivity data are compared with those of other membranes published in the literature and it is found that PERVAP™ 4060 has the highest PSI value and its other parameters are also among the best. Our experimental data are evaluated with the pervaporation model of our improvement and it is found that the model can be applied also for both organophilic and hydrophilic pervaporations. The hybrid separation system is rigorously modelled with ChemCAD and optimized with the dynamic programming optimization method. The objective function of the hybrid system is the total annual cost but its energy consumption is also investigated. It can be determined that this hybrid process, that is, the combination of organophilic and hydrophilic pervaporations is capable for the separation of isobutanol and water and it can become the alternative of distillation based separation. Considering our results it can be assumed that the combination of the organophilic and hydrophilic pervaporations opens new horizons for the membrane processes.

2.3 Definition of the "membrane flash index" which provides an easy and simple comparison of pervaporation and distillation,

Chemical process design is the creative step of engineers which should be supported by different computer aided design tools. Such tools should be simple and easy to use since process synthesis often means the investigation of a huge number of alternatives. While designing separation of liquid mixtures distillation and pervaporation are usually simultaneously considered since pervaporation is frequently taken into account as an alternative for distillation. To easily compare the efficiencies of continuous pervaporation and distillation, we propose a new and simple method, the so called Membrane Flash Index (MFLI). The comparison is based upon vapor-liquid equilibrium data and the permeation data of pervaporation therefore it can be plotted on a common chart in the case of binary mixtures.

The determination of the Membrane Flash Index (MFLI), the ratio of y_i^{PV} (vapor mole fraction after pervaporation) and $y_i^D[VLE]$ (the vapor mole fraction of a simple flash unit) can give a novel evaluation index of comparison of pervaporation with distillation that is MFLI:

$$MFLI = \frac{y_i^{PV}}{y_i^D[VLE]}$$

The permeation values of organophilic and hydrophilic pervaporations can be calculated with the help of known separation factors and feed concentrations. MFLI is dimensionless and can be determined by dividing the permeate concentration with the corresponding vapor equilibrium data obtained from a simple flash distillation. Only feed concentration, separation factor and refereed equilibrium data are necessary for the calculations. If MFLI is lower than one, the application of pervaporation can be worse than that of the distillation. In our study the efficiency of pervaporation and distillation are compared using three mixtures, methanol–water, ethanol–water and isobutanol–water. After determining MFLI for different types of membranes, it can be concluded that the separation capability of hydrophilic membranes is significantly higher than that of the organophilic ones. Apart from azeotrope braking, MFLI, as a single number, gives clear information about the separation capabilities of pervaporation and distillation in the course of process design.

2.4 Determination of the thermodynamically best operation range and controllability of dividing wall columns

This part of our research is about dividing-wall distillation columns (DWCs) with upper and lower partitions (Figure 3). These kind of columns are now the renaissance of the dividing wall columns, originally proposed by Petlyuk[2] and Kaibel[3].

Thermodynamic efficiencies and heat demands are investigated to offer a more complex point of view about distillation technologies. Rigorous simulations of nine distillation systems are completed and the results are evaluated. Among the separation systems there are conventional direct and indirect distillation systems and energy-integrated ones, that is, DWCs with upper and lower partition, columns with side stripper or side rectifier, the fully thermally coupled distillation column (FTCDC), the sloppy system, and a direct sequence with backward heat integration (DQB) are examined using three different alcohol mixtures. Results are obtained from rigorous simulations using exergy analysis. Thermodynamic efficiencies are in agreement with the expectations based on previous researches. Based on the thermodynamic efficiencies and heat demands the direct sequence with backward heat integration proved to be the most suitable distillation technology for the mixtures examined. The DWC with upper partition shows also promising behavior.

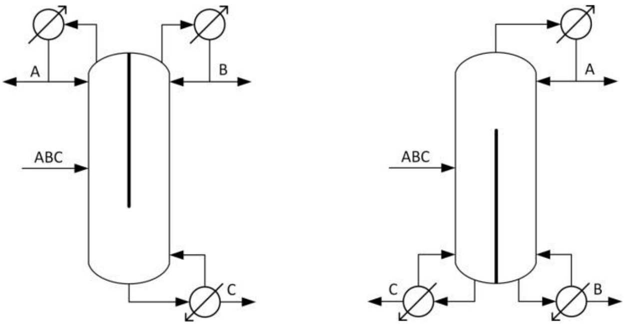

Figure 3, Dividing wall columns with upper and lower partitions

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[2] Petlyuk, E B., V. M. Platonov and D. M. Slavinskij (1965). Thermodynamically Optimal Method for Separating Mul- ticomponent Mixtures. Int. Chem. Eng. 5(3), 555-561.

[3] Kaibel, G., Distillation columns with vertical partitions. *Chemical Engineering & Technology* **1987,** 10, (1), 92-98

In the frame of the study of the controllability properties of conventional distillation sequences and dividing-wall columns with upper and lower partitions (DWCs) we used the controllability analysis methodology based on the Control Design Interface (CDI) module of Aspen Dynamics to obtain the state space representation of the studied systems. The frequency dependent controllability indices are calculated by Matlab on the basis of the matrices of the transferred state space representation. The study includes the examination of the conventional direct and indirect sequences and two DWCs systematically generated from the corresponding conventional sequences. Case studies are completed using ternary alcohol mixtures with different eases of separation. Results show that conventional distillation sequences have more favorable controllability properties than those of the DWCs if direct separation and mixtures with symmetrical ease of separation are considered. In the cases of mixtures with non-symmetrical ease of separation, the indirect separation the DWC with lower partition show practically similar controllability features than those of the corresponding conventional sequences.

2.5 Comparison of the energy requirement of rectification with energy integration and pervaporation.

The comparison was completed on an important separation problem.

Isobutanol-water separation is increasingly important in the field of biofuels and process wastewater treatment. There are many options for the separation and they differ in their efficiency, operational and investment costs, robustness, development level and environmental impact.

Five separation structures are compiled using distillation, both organophilic and hydrophilic pervaporation and hybrid separation units consisting of distillation and pervaporation. Heat integration is also considered. The different alternatives are modelled in professional flowsheeting environment. Life cycle assessment, economic analysis and PEST analysis are completed to evaluate and compare the five alternatives.

The feed stream to be separated has the composition of 7 wt% isobutanol 93 wt% water that corresponds to the mixture of the phase split due to the limited solubility. Two product purities are considered, 98.8 and 99.9 wt%.

In the case of distillation the heat integration is also considered, that is, the feed is preheated with the bottom flow of the distillation column. The heat integration significantly improves the efficiency of the distillation and makes it for practically the best alternative. Similar efficiency can be obtained with hybrid separation, that is, the combination of distillation and pervaporation.

The pure pervaporation that is the combination of organophilic and hydrophilic pervaporation can be competitive only at not too sharp product purities because of the modest separation factor of the organophilic pervaporation membranes. In case of sharp separations, the organophilic pervaporation is replaced with the heat integrated distillation.

After this study we have the conclusion that energy integration can beat the pervaporation that is believed to be the replacement of distillation. So it is still far….

3.) Algae based technology to capture and utilize CO_2

The algae based technologies have been studied for a long time. One of its merit is that algae can turn the CO_2 into oxygen developing also itself via photosynthesis. Therefore it has a great interest.

Our developed approach applies a new idea, that is, we do not dry the algae but use hydrothermal gasification. Such an approach is more economic that other ideas where for the sake of extraction the algae has to be dried.

The two solutions are presented in Figure 4. The so called dry route and our way, the hydrothermal gasification way we studied and improved.

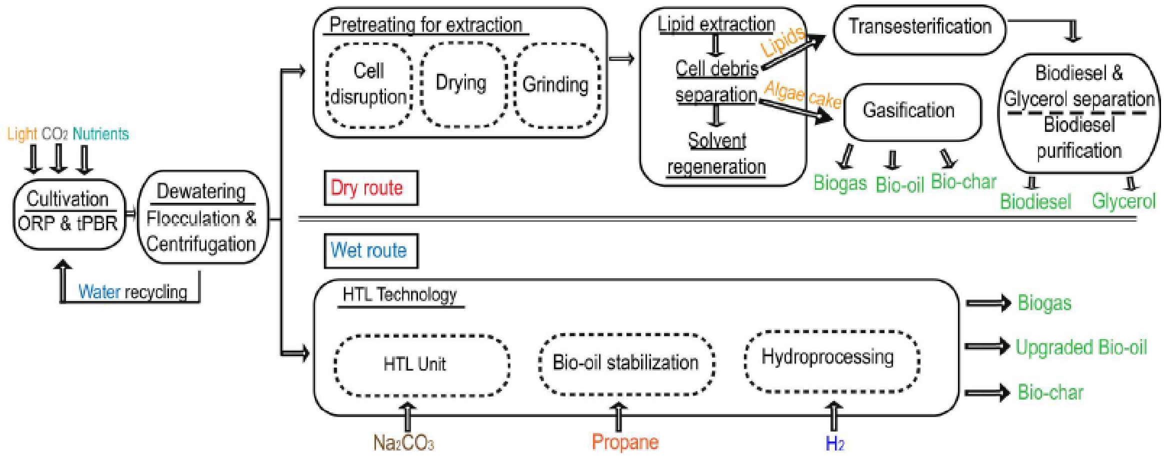

Figure 4, Concepts of algae utilization technologies

Hydrothermal – high pressure and temperature – technologies (including hydrothermal gasification and hydrothermal carbonization) were investigated for the valorization of wet microalgae biomass (Chlorella vulgaris) and organic wastes.

The transformation of microalgae into bio-fuels is limited due to the dilute algae suspension that is derived from the culture broth. Conventional thermochemical processing technologies (e.g., pyrolysis, atmospheric gasification) and transesterification of triglycerides require the prior drying of wet feedstock. This results in elevated energy demands that restrict the efficient operation of third generation biorefineries. In order to bypass this conversion related technological bottleneck, hydrothermal processes were utilized for the valorization of wet organic feedstocks that allow the elimination of energy intensive pre-drying processes.

Hydrothermal gasification (HTG) is a promising technology for the decomposition of organic materials with high moisture content above the supercritical point of water (T_c=374°C and p_c=221 bar). In our investigation it is found that the biological composition of microalgae cells can influence the biogas quality that produced via the hydrothermal process. Throughout the cultivation step the lipid and carbohydrate content can be affected by changing light intensity and aeration levels. that higher methane yield can be reached by the hydrothermal treatment if the lipid content of the biomass increased during the upstream process. While in case of algae samples within the biological composition shifted through targeted cultivation towards higher carbohydrate content result in higher H_2 mole fraction.

Hydrothermal carbonization (HTC) is also investigated for the valorization of organic waste derived from industrial application (wastewater treatment plant). HTC is a suitable thermochemical process to convert inhomogeneous organic wastes into hydrochar (HC) which is a multifunctional value-added product. HC can be used as solid biofuel, adsorber, soil amendment and catalyst. Waste disposal and management are becoming a more and more important subject to achieve long-term environmental sustainability goals. Within the framework of circular economy, the waste-to-hydrochar concept has a high importance to recover energy, decrease the application of non-renewable energy vectors and to support the creation of energy security. In our investigation multi-objective optimization was carried out to determine ideal reaction conditions for the following cases:

- efficient solid biofuel production with high quality,
- efficient solid blending component production with high quality,
- coal blending component production with high feedstock conversion,
- efficient HC production, high feedstock conversion and decreased TOC content of the co-produced process water.

A novel process – co-Hydrothermal Gasification - was developed to increase the gas yields and component selectivity of HTG. It is found that the application of co-gasifying agents expands the number of influencing parameters in hydrothermal gasification since both the blending component composition and blending concentration were found to be significant factors regarding the yields of co-HTG. Thus, HC blending components improve the controllability of biogas production. Moreover, the application of HCs results in similar gas yields as it was reported in former studies that investigated biomass valorization via catalytic hydrothermal gasification. Consequently, hydrochar blends outperform homogeneous and heterogeneous catalysts since they are cheap and offer similar HTG gas yields without having deactivation and thermal decomposition difficulties during the operation.

It is important to note that a liquid fuel production company is highly interested in our novel biorefinery concept.