

Experimental Investigation, Analysis and Optimisation of Hybrid Separation Processes

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Problem addressed

In recent years, the chemical process industry has shifted its attention to the development, implementation, and application of integrated processes that combine separation and reaction inside a single unit. Benefits, such as reduced equipment and plant sizes, and improved process efficiency and economy are responsible for these recent trends. Reactive distillation is an important example of a reactive separation process and used, especially for equilibrium reactions like esterifications, ester hydrolysis, and etherifications. The combination of reaction and separation within one zone of the reactive distillation column is a well-known alternative to conventional processes with sequential reaction and separation steps. In several cases, non-ideal aqueous organic mixtures are formed, which tend to form azeotropes. These azeotropes contain either the desired products and/or reactants, and, unfortunately, they require further separation steps. Aside from classical separation processes like extractive, heteroazeotropic, pressure-swing distillation and molecular sieves, membranes can be applied. Membrane separations, such as pervaporation and vapour permeation, overcome the limitations set by azeotropes since they are selective and not limited by the vapour-liquid equilibrium [MEL04]. Consequently, a combination of both unit operations in a so-called hybrid separation process consisting of a membrane-assisted reactive distillation unit contributes to a sustainable process improvement due to arising synergistic effects, and it reduces investment and operational costs. Despite these advantages, the potential of membrane-assisted reactive distillation has yet to be fully exploited due to a lack of available design methodologies. Moreover, the interactions that occur in the hybrid process require detailed process know-how of the stand-alone units and the combined apparatuses. A reliable process development requires advanced tools for predictive simulation that allow the full potential of the hybrid process technology to be exploited. This motivation has directed the present thesis, which covers the experimental investigation, process analysis, and optimisation of a hybrid process consisting of reactive distillation and vapour permeation (cf. Figure 1).

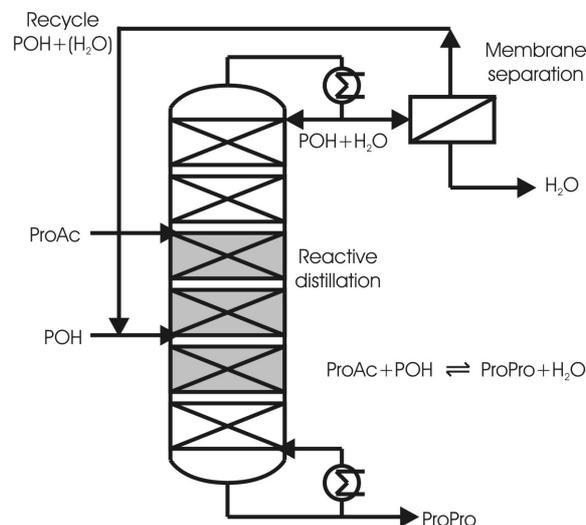


Figure 1: Reactive distillation column with a membrane separation located in the distillate stream.

The work was conducted in the framework of the EU-project "INSERT-*Integrating Separation and Reaction Technologies*", which was a specifically targeted research project (STREP) funded by the European Commission within the 6th Framework Programme, Contract-No: NMP2-CT-2003-505862. One of the six investigated test systems included the esterification of 1-propanol and propionic acid to *n*-propyl propionate and water in a membrane-assisted reactive distillation column. This system is the subject of the present thesis.

State of the art

Hybrid separation processes have attracted considerable attention over the years as a synergistic interaction of two unit operations that contrasts the sequential configuration of different apparatuses. Moreover, the smart combination of mature unit operations, such as (reactive) distillation or batch reaction, with the membrane processes vapour permeation or pervaporation are promising alternatives to meet the economical and ecological demands of the process industry [NOB05, JAN05]. Therefore, hybrid separation processes are an interest both academically and industrially.

Process intensification comprises a "novel equipment, processing techniques, and process development methods that, compared to conventional ones, offer substantial improvements in (bio)chemical manufacturing and processing" [MOU08]. One of the most promising ways to implement process intensification is to deliberately integrate different phenomena or operations. Therein, the chemical process industry has demonstrated a growing interest in the development of integrated processes that combine reaction and separation mechanisms into a single [NOE03]. Reactive distillation is the simultaneous realisation of reaction and multistage distillation in one apparatus, and it is one of the most important industrial applications of the integrated process concept. Reactive distillation belongs, in accordance to Agar [AGA99], to the concept of multifunctional reactors, and it can be regarded as a highly complex system due to the simultaneous presence of a vapour, liquid, and solid phase. Reactive distillation has attracted considerable attention, especially for equilibrium limited liquid phase reactions, which are normally conducted with a large excess of one of the reactants.

Reactive distillation is an old idea that has received renewed attention in recent years [MAL00]. The first patent for the application of a homogeneous catalysed esterification was filed in 1921 by Backhaus; however, reactive distillation is contemporarily regarded as an established process technology, and Harmsen has referred to reactive distillation as a front-runner to industrial process intensification [HAR07]. Several reviews by Hiwale et al. [HIW04], Schoenmakers and Bessling [SCH03], and Stankiewicz [STA03] comprehensively discuss the potential industrial applications and perspectives of reactive distillation processes.

Membrane-based technology is currently regarded as a new frontier of (bio)chemical engineering. Even though membrane processes continue to be of increasing importance contemporarily, the usage of such membranes is not a novel method. The breakthrough of membrane technology can be related to the production of high-flux asymmetric polymer membranes by Loeb and Sourirajan [LOE63]. The first industrial application of a pervaporation plant was constructed in Brasil in 1983 for the dewatering of ethanol. Comprehensive research and several technological improvements in the field of vapour permeation (VP) and pervaporation (PV) have enabled the utilisation of membrane technology in the chemical industry. Presently, more than 100 industrial plants are operating with the purpose of dewatering organic solvents [KRE04].

Application	Reaction	Process	Membrane	Module type	Catalyst	Ref.
MTBE	Est.	PV	PVA membrane	Unspecified	Ion-exchange resin	Matong et al. [MAT94]
Unspecified	Est.	PV	Pervap TM 1137, 1610	Unspecified	Unspecified	Bart & Reiel [BAR97]
ETBE	Eth.	PV	Polyion	Hollow-fiber	Amberlyst TM 16	Yang & Goto [YAN97]
Trimethylborate	Est.	VP	Unspecified	Unspecified	Unspecified	Mans & Brützke [MAU02]
TAME	Eth.	PV	NaA zeolite	Tube	Amberlyst TM 16	Aionache & Goto [AIO03]
n-Butyl acetate	Transest.	PV	Pervap TM 2255-40, -60, -80	Circular flat-sheet	Amberlyst TM 16	Steinigeweg & Greshing [STE04]
Fatty acid ester	Est.	PV	Pervap TM	Unspecified	Ion-exchange resin	von Seula et al. [VSCA05]
n-Butyl acetate	Est.	PV	PEBAX® 2533	Unspecified	Amberlyst TM	Liu et al. [LIU06]
n-Butyl acetate	Transest.	VP	Pervap TM 2256, 2255-30, -80; sPEEK; PVA/HO ₂	Test cell	Amberlyst TM	Brückmann et al. [BRÜ08]

Table 1: Summary of surveyed literature regarding hybrid processes comprising reactive distillation and membrane separation (Est. = Esterification, Eth. = Etherification, Transest. = Transesterification, VP = Vapour Permeation, PV = Pervaporation)

Hybrid separation processes are characterised in the frame of this work by a coupling of at least two different unit operations, which together solve a separation problem in one process step in separated devices simultaneously, based on different physical phenomena [KRE04]. The interactions of both unit operations entail strong synergies, which contrast sequentially configured apparatuses. Hence, the limits of stand-alone unit operations, such as distillation, extraction, crystallisation, membrane separation, and chromatography can be overcome by their smart combination. Despite their advantages, hybrid separation processes are contemporarily rarely introduced in industry due to a general scepticism with respect to new process types, a lack of sound and reliable design methodologies, and a lack of detailed process know-how arising from the increased complexity of combined unit operations.

The combination of continuous distillation with the membrane processes pervaporation and vapour permeation exhibits a significant economical potential; therefore, it has been actively investigated in academia and industry [SOM04, GOR07]. This hybrid process uses the strengths of distillation and overcomes its thermodynamic limitations through the advantages of membrane separation units, which operate independently of the vapour-liquid equilibrium. The combination of these unit operations can facilitate the development of new process alternatives and also de-bottleneck existing distillation columns to increase process capacity.

The work conducted thus far in the area of hybrid processes involving reactive distillation and membrane separation is summarised in Table 1.

The presented short state of the art illustrated clearly that currently, hybrid processes, consisting of a combination of reactive distillation and membrane separation, are an interesting and promising process technology. Despite all its advantages, membrane-assisted reactive distillation is rarely used because of a lack of available design methodologies. The complex interactions in the hybrid process require an in-depth understanding of both stand-alone units and coupled apparatuses. Hence, to fully exploit the potential of hybrid processes, reliable process development requires advanced modelling and simulation tools.

Summary, Key innovations and applications, implementations and results

Integrated processes, such as reactive distillation, which are combining reaction and separation in one apparatus, represent an important application in the frame of process intensification as one of today's most significant trends in chemical engineering and process technology. Additionally, the combination of different unit operations to a hybrid separation process can lead to a sustainable increase in the entire process performance due to arising synergy effects. Hybrid separation processes are characterised by a coupling of at least two different unit operations, which together solve a separation problem in one process step in separated devices simultaneously, based on different physical phenomena. In the presented thesis, a new methodology for the development and analysis of hybrid separation processes was developed (cf. Figure 2).

The proposed design methodology was applied to the synthesis of *n*-propyl propionate by esterification of propionic acid and 1-propanol using a hybrid separation process comprising the unit operations reactive distillation and membrane separation. Membrane-assisted reactive distillation can be considered as an industrially accessible and developed technology, since it consists of two units that are nowadays broadly applied on a commercial scale.

However, integration of a pervaporation or vapour permeation unit requires an in-depth process knowledge to find the optimal process configuration and to exploit the full potential of these interesting process technology. The *n*-propyl propionate synthesis was heterogeneously catalysed by a surface-sulfonated cation exchange resin, Amberlyst® 46, from Rohm and Haas which is a tailor-made catalyst for esterifications since competing side product formations are suppressed. Important catalyst properties, namely the amount of dry catalyst per meter catalytic packing and the concentration of active sites were determined. Based on a long-term capacity analysis, it could be shown that the catalyst activity remains for 1-propanol and propionic acid at a constant level after conditioning. Contrarily, suspension of catalyst in *n*-propyl propionate led to a strong irreversible deactivation, although the responsible mechanisms are unknown.

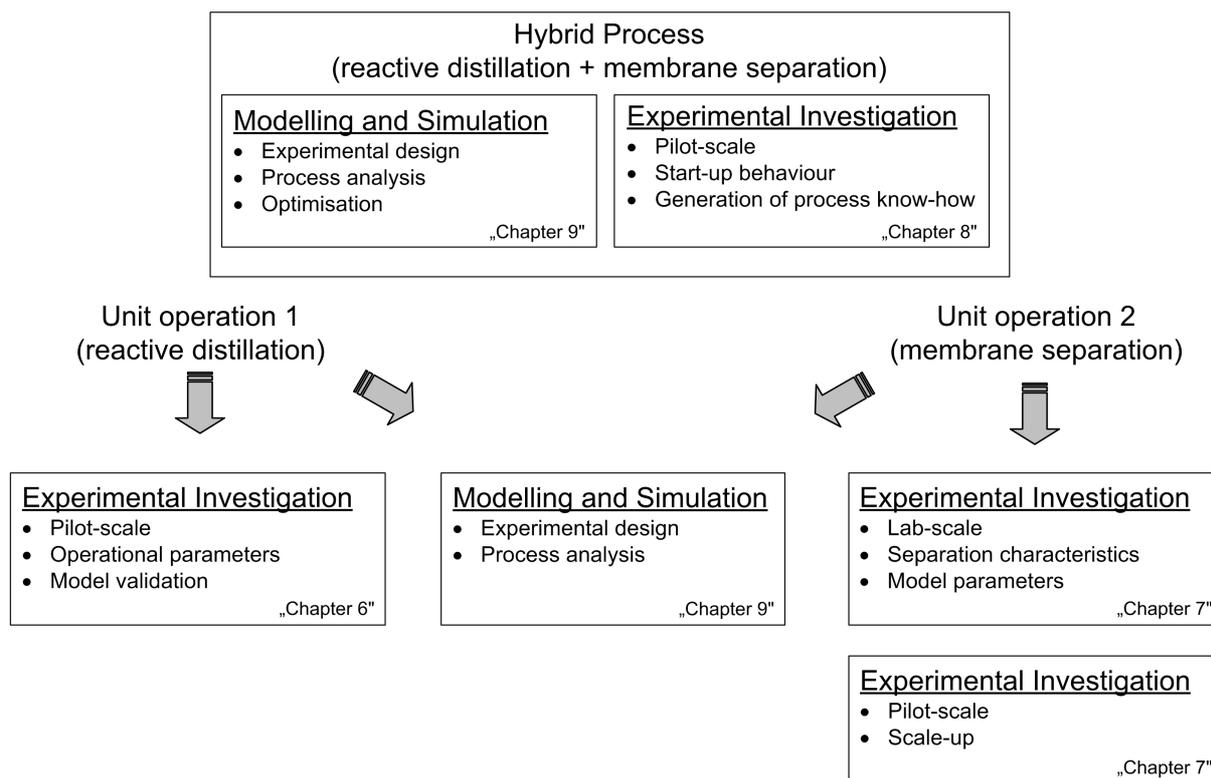


Figure 2: Methodology of this work.

In order to prove the feasibility of the membrane-assisted reactive distillation concept, the reactive distillation column and vapour permeation plant were operated independently in a first step and connected for the first time to a hybrid process in a later stage. The aim of the conducted experiments was to demonstrate the feasibility of the innovative process and to provide reliable data for the validation of detailed mass transfer models for both reactive distillation and membrane separation.

Reactive distillation experiments were performed in a stand-alone reactive distillation column using a structured catalytic packing, Katapak™-SP 11, in the reactive zone and a conventional wire-gauze packing, Sulzer BX™, in the stripping and enrichment part (cf. Figure 3). Based on a computer aided experimental design, the conducted reactive distillation experiments covered a broad range of decisive parameters. These independently investigated operating parameters included: the distillate-to-feed ratio, reflux ratio, molar feed ratio of 1-propanol feed to propionic acid feed as well as the total feed flow rate. Results of the extensive reactive distillation experiments demonstrate that the synthesis of *n*-propyl propionate in a reactive distillation column is feasible. No di-*n*-propyl ether as the main side product was detected in any experiment. Furthermore, the results indicate that the distillate-to-feed ratio and the column load show the highest influence on the operating behaviour of the reactive distillation column in the investigated operating window. The surface-sulfonated catalyst Amberlyst® 46 was used for 500 operating hours in the catalytic packing during an experimental period of 24 months and did not show significant loss of its catalytic activity. The quality of the experimental results could be strongly enhanced in this thesis by application of an online and offline data reconciliation procedure. Key aspects for a proper description of reactive distillation processes were introduced and thoroughly discussed. A detailed non-equilibrium stage model based on the Stefan-Maxwell equations was used for the simulation of the integrated process.

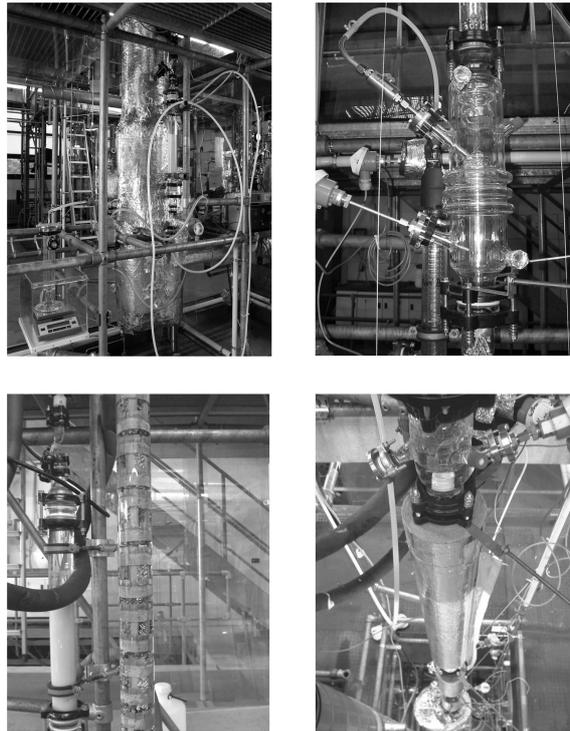


Figure 3: Reactive distillation plant at the Laboratory of Fluid Separations, TU Dortmund. Top, left: reboiler; top, right: distributor with feed inlet; bottom, left: glass segment filled with Katapak™-SP 11 packing elements; bottom, right: first isolation layer.

It can be noted that the experimental data were in excellent agreement with the simulated results, confirming the reliability of the fully predictive process model which uses zero subsequent adjustable model parameters (cf. Figure 4).

Furthermore, a systematic analysis of the separation of aqueous-organic mixtures by vapour permeation using flat-sheet membranes was accomplished in this thesis. By means of binary and ternary vapour permeation experiments with a multipurpose lab-scale plant and an available membrane area of $A_{\text{memb}} = 161.4 \text{ cm}^2$, it could be demonstrated that the applied hydrophilic PVA membrane Pervap™ 2201 (D) from Sulzer Chemtech is suitable for the dewatering of the distillate stream of the reactive distillation column.

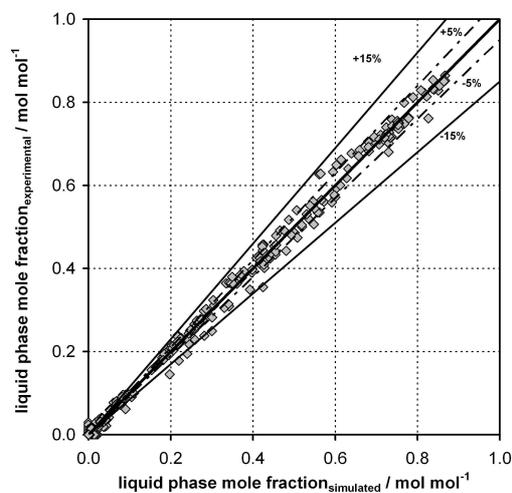


Figure 4: Parity plot of the simulated and reconciled experimental molar fractions of all four components in the liquid phase.

The membrane works independently of the vapour-liquid equilibrium and is stable at the chosen operating conditions. The separation characteristic of the polymeric membrane identified the influence of the important operational parameters on the performance of the membrane unit. In the measured concentration range, the membrane shows a high selectivity and high fluxes. Based on the characterisation of the membrane, a semi-empirical modelling approach was applied to calculate the transmembrane flux. The largest impact on the permeate flux was caused by the feed concentration of the favourable permeating component water and the degree of superheating. Decreasing water concentrations yield to a decrease of the permeate flux and membrane selectivity.

The scale-up of the membrane was analysed based on binary 1-propanol/water experiments in a pilot-scale plant with a membrane area of 0.5 m^2 (cf. Figure 5).

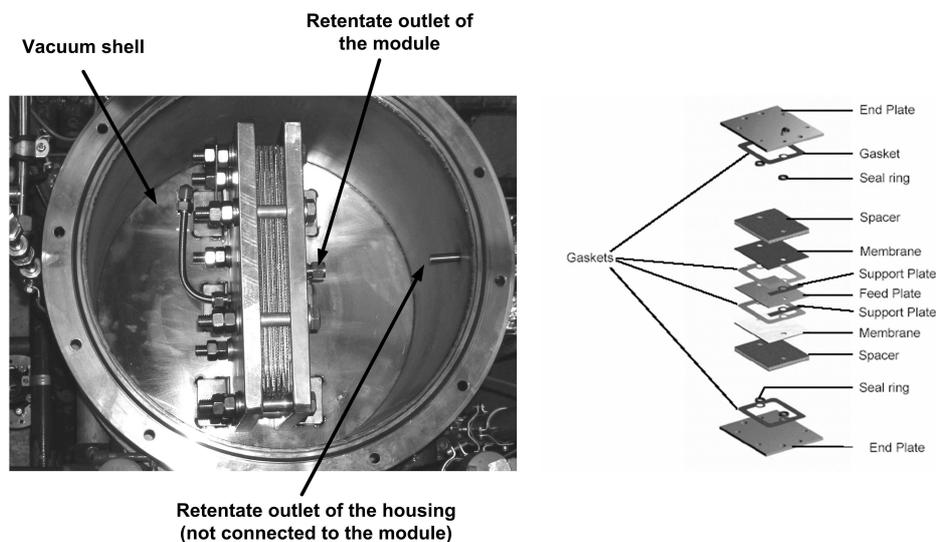


Figure 5: Pilot-scale membrane module (left) and its explosion drawing (right, [OHL06]).

In comparison to test cells with a smaller membrane area, a significant dewatering occurred in the pilot-scale module, changing the permeate fluxes along the membrane. Despite the increased complexity, a successful scale-up of the vapour permeation process was demonstrated. One modelling approach can be used for the simulation of the mass transfer in the membrane module in both scales (cf. Figure 6).

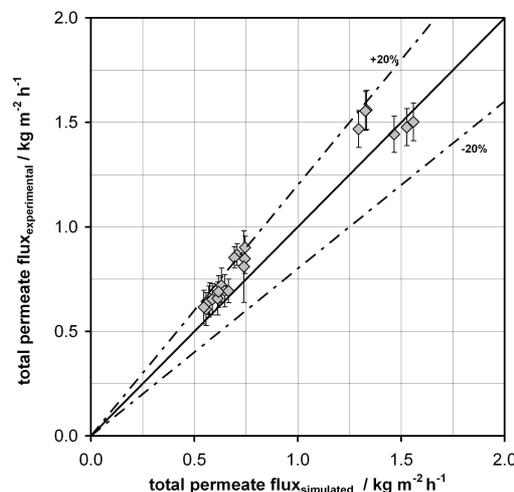


Figure 6: Comparison between the experimentally determined and simulated permeate flux of the pilot-scale membrane module.

For the first time, experimental results of the fully coupled unit operations are presented. The complex interactions of both plants required the development of an advanced start-up strategy. Results of the successful experiment with fully coupled unit-operations proved that the hybrid process concept is feasible. The pure 1-propanol feed to the column could be reduced significantly by a placement of the membrane into the column distillate stream, while the ester purity in the bottom stream increases. Moreover, the convincing results showed that the simulation of the hybrid process based on detailed process models for both stand-alone unit operations is in excellent agreement with the experiments (cf. Figure 7).

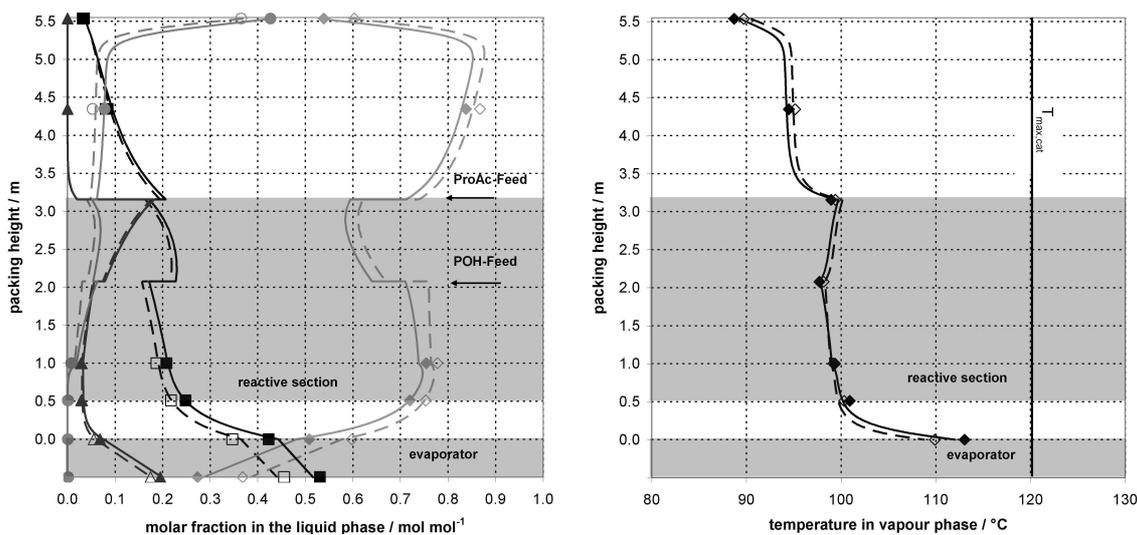


Figure 7: Comparison between the experimental and simulated composition and temperature profile: liquid phase molar fraction (left) and temperature profile of the vapour phase (right) for the fully coupled hybrid experiment with sequential configuration (dashed lines, open symbols) and closed recycle (solid lined, filled symbols). The lines represent the simulation results, the symbols the experimental values.

The most common modelling depths for the description of reactive distillation processes, namely the non-equilibrium stage model, the equilibrium stage model taking into account reaction kinetics and the equilibrium stage model assuming chemical equilibrium, were compared with each other. One major result of this theoretical study is that the equilibrium stage model assuming chemical equilibrium is not sufficient for a proper description of the *n*-propyl propionate synthesis in a reactive distillation column at laboratory and pilot-scale. The non-equilibrium stage model and the equilibrium stage model with reaction kinetics exhibit qualitatively similar results over a broad range of catalyst volume fractions. The simulation study shows that accurate reaction kinetic data is crucial for investigation of the reactive distillation process in laboratory and pilot-scale columns. Industrial-scale columns with a high catalyst volume fraction show a lower sensitivity to the reaction kinetic data.

Simulations studies with the validated membrane model illustrated the impact of feed temperature, since an increase in the degree of superheating yields to a strong decrease in membrane separation capabilities. Furthermore, it is important to take the pressure decrease for the investigations of industrial-scale vapour permeation modules into account.

The analysis of the hybrid separation process shows an even higher complexity in comparison to stand-alone unit-operations due to the dependency of both processes. Thus, the presented validated process models for both units were linked to enable a theoretical analysis of hybrid separation processes. Comprehensive simulation studies illustrated the influence of structural and operational parameters on process performance. The analysis of the variation of the reflux

purity as the decisive operational variable for the performance of the hybrid process showed contrary effects of reboiler heat duty and required membrane area, which resulted in a classical optimisation problem. Therefore, a rigorous optimisation algorithm for optimisation of hybrid processes based on detailed mass transfer models was presented. The applied evolutionary optimisation algorithm was based on a "modified differential evolution" approach which was extended in the scope of this work to handle complex steady-state processes. Results of a case study comprising the optimisation of the hybrid separation process in pilot-scale proved the successful applicability of the now available optimisation package (cf. Figure 8).

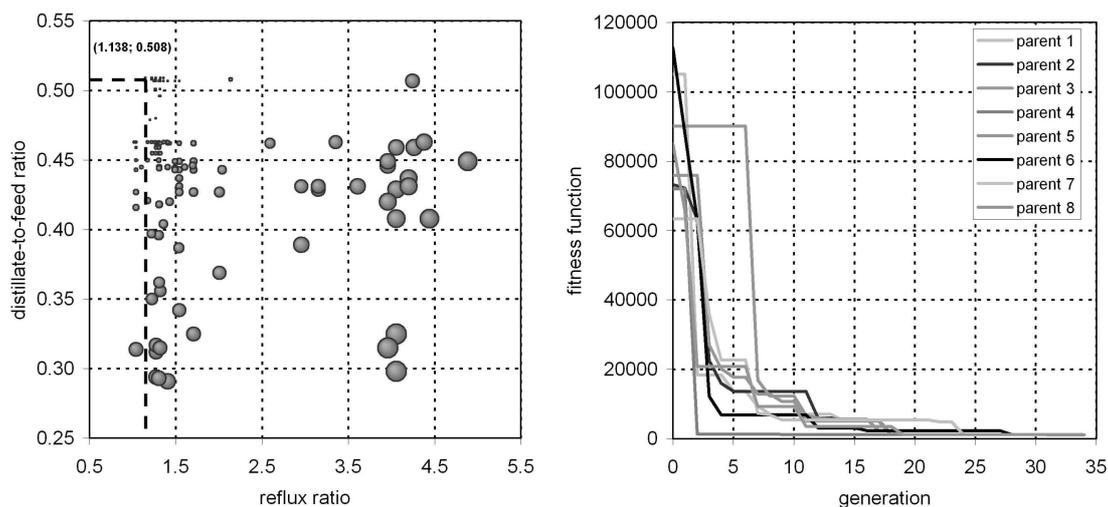


Figure 8: Progress of the evolutionary algorithm

It can be stated that a consideration of process economics as well as structural variations are mandatory for a consequent continuation of process optimisation. Therefore, it is necessary to take into account operating and investment costs of both unit operations. Moreover, by the now available validated model library in combination with the superposed evolutionary algorithm, it is possible to analyse the influence of the choice of modelling depth on result of a rigorous process optimisation.

Based on the conducted extensive research and development it can be concluded, that the present work contributes to an exploitation of the dormant potential of hybrid separation processes.

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