EXPERIMENTAL INVESTIGATION OF REACTIVE DISTILLATION IN COMBINATION WITH MEMBRANE SEPARATION

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INTRODUCTION

Reactive distillation (RD) is a classical example of integrated processes in which reaction and separation is combined within one single apparatus. An industrial relevant application of RD is the esterification reaction in which non-ideal aqueous-organic mixtures are produced. Their dewatering through a membrane leads to process intensification and allows for reducing investment and operational costs [1].

In this work, the esterification of propionic acid (ProAc) with 1-propanol (POH) to n-propyl propionate (ProPro) and water (H_2O) is investigated:

$$C_3H_8O + C_3H_6O_2 \iff C_6H_{12}O_2 + H_2O \tag{1}$$

The reaction is heterogeneously catalysed by a strongly acidic ion-exchange resin. The chemical system shows complex phase behaviour with several binary and ternary azeotropes. Boiling points of the pure components as well as the azeotropic data of the system are shown in Table 1.

PROCESS DESCRIPTION

Reactive distillation represents probably one of the most important applications of an integrated multifunctional process unit, combining reaction and separation in one zone of a column. Especially for equilibrium limited reactions, reactive distillation can considerable improve the process performance. Higher conversions and selectivities may reduce investment and operating costs significantly.

One possible process alternative for the n-propyl propionate synthesis is the removal of the desired product (ProPro) at the bottom of the column, while at the top an almost azeotropic aqueous-organic mixture (POH/H_2O) is obtained. Here, the coupling of the reactive distillation column with a membrane module generates a reactive hybrid process (Figure 1).

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Table 1. Boiling points of pure components and azeotropic data of the n-propyl propionate system at 1 atm [2,3]

	T_b [°C]	type	x_{POH} [−]	x_{ProAc} [−]	x_{ProPro} [−]	x_{H_2O} [−]
POH	97.2	–	1.0	–	–	–
H_2O	100.0	–	–	–	–	1.0
ProPro	122.9	–	–	–	1.0	–
ProAc	140.9	–	–	1.0	–	–
POH-ProPro-H_2O	86.2	het	0.350	–	0.130	0.520
POH-H_2O	87.6	hom	0.432	–	–	0.568
ProPro-H_2O	90.0	het	–	–	0.350	0.650
ProAc-H_2O	99.9	hom	–	0.050	–	0.950

A hydrophilic membrane unit is located in the distillate stream. The water depleted retentate is recycled back to the column while the permeate is removed out of the process.

OBJECTIVES

Related to the heterogeneously catalysed esterification on 1-propanol with propionic acid in a RD column no data is available in the open literature. Therefore in this work

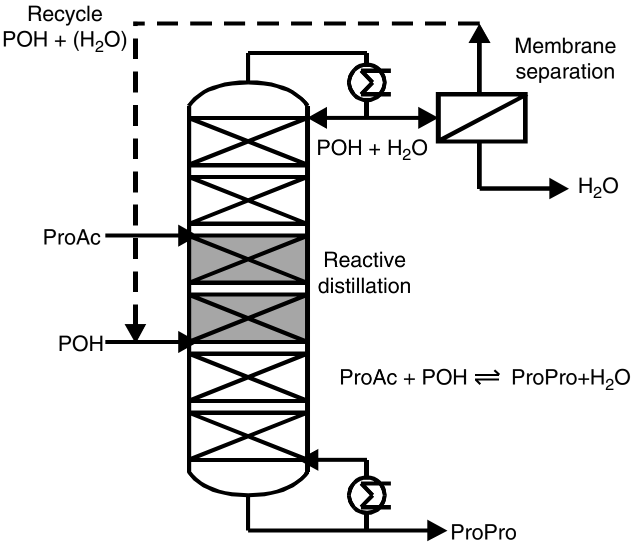

Figure 1. RD column with a membrane in the distillate stream

the feasibility of both stand-alone unit operations, reactive distillation and vapour permeation, is demonstrated. The influence of decisive operating conditions (molar feed ratio, reflux ratio, distillate-to-feed ratio) is investigated and a data reconciliation is applied to reconcile the RD experiments and to provide reliable experimental data for further simulation studies.

Additionally, vapour permeation experiments are presented. The results demonstrate the suitability of the used polymeric flat sheet membrane (Pervap 2201 D from Sulzer Chemtech) for the investigated case study.

REACTIVE DISTILLATION EXPERIMENTS

Reactive distillation experiments were carried out in a glass column with an inner diameter of 50 mm at atmospheric pressure. The set-up has a separation section below and above the reactive section whereas the total packing height was 5.5 m (Figure 2). The characteristics of the used pilot plant are summarised in Table 2.

The immobilisation of the heterogeneous catalyst, Amberlyst 46 (Rohm & Haas), inside the reactive section was achieved by the structured packing Katapak-SP (type SP 11, Sulzer Chemtech). Amberlyst 46 has its acidic active sites (sulfonic-acid groups)

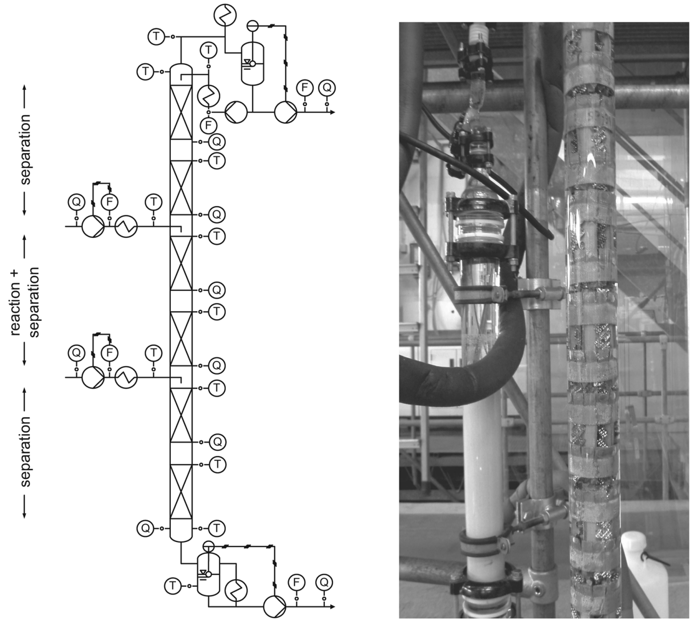

Figure 2. Scheme of catalytic distillation column (left), Installation at the Universität Dortmund (right)

Table 2. Pilot plant characteristics

	Pilot plant column
Column diameter	50 mm
Rectifying section	2.4 m (Sulzer BX)
Reactive section	2.6 m (Katapak-SP 11)
Stripping section	0.5 m (Sulzer BX)
Pressure	Atmospheric
Condenser type	Total condenser

present only at the surface of the styrene-co-divinylbenzene matrix. This catalyst is tailor-made for esterifications, because competing side product formations, e.g. etherification and dehydration of the alcohol are suppressed [4, 5, 6].

Mass flow rates of both feed, distillate and bottom streams were measured directly with balances, while a calibrated coriolis type flow meter was used to determine the reflux flow rate. Vapour temperatures were measured at each distributor using PT-100 thermocouples. The liquid samples were analysed by gas chromatography (FID) and Karl-Fischer titration to determine the mass-fraction of all components.

DATA RECONCILIATION

Data reconciliation adjusts process parameters and concentrations by having them satisfy mass and component balances and reaction rates as boundary conditions (BC). There, the measured variables are varied within their limits of the experimental error. The general formulation of the data reconciliation problem with the use of a weighted least square (WLS) objective function, ϕ, is posed as:

$$\phi = \min \sum_{i=1}^{n} \frac{(x_{i,\exp} - x_{i,\text{reconciled}})^2}{\sigma_i^2}. \tag{2}$$

During an experiment the data reconciliation was performed to verify, if the column was in a steady state condition ("Online Data Reconciliation"). If the RD column reached a steady state, three column profiles were taken in an interval of 60 minutes each.

EXPERIMENTAL DESIGN AND PROCEDURE

The experiments demonstrate the feasibility to synthesise the n-propyl propionate in a RD column. They were designed in order to show the influence of relevant operational parameters like the molar feed ratio as well as the distillate-to-feed (D/F) and reflux ratio (RR) on the column performance. The experimental program is illustrated in Figure 3. Realised experiments are marked with filled symbols and numbered.

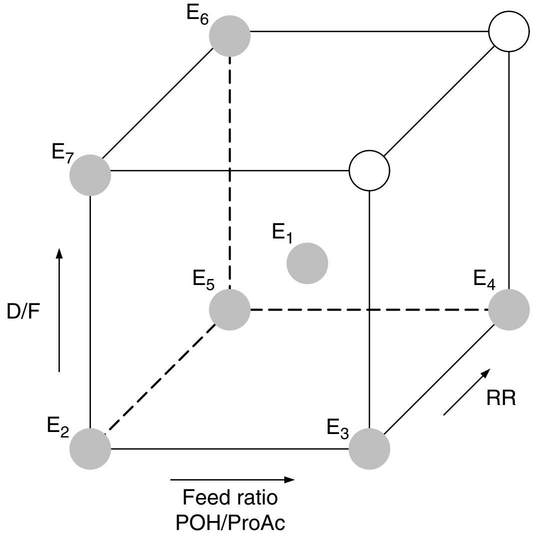

Figure 3. Experimental design

Propionic acid was fed above the reactive section (at 3.1 m), while the 1-propanol was fed below it to ensure a counter current contact between both reactants. The total feed flow rate was kept constant at 2.0 kg/h for all experiments while the reflux ratio, RR, was varied from 2.0–2.5 and the distillate-to-feed ratio in the interval of 0.34–0.45 kg/kg. An excess of 1-propanol was necessary to provide a high conversion of the propionic acid and prevent the formation of an additional liquid phase. Therefore, the molar feed ratio of 1-propanol and propionic acid was varied between 2.0 and 2.45. The operating conditions as well as mass streams and liquid compositions of distillate and bottom stream are summarised in Table 3 for all reconciled experiments.

Results of the performed data reconciliation are shown in Table 4 and Table 5. All experiments beside E6 show a high accuracy and therefore they can be regarded as reconciled.

Figure 4 shows the liquid phase molar fraction and vapour temperature profiles along the packing for experiments E4. It proves, that the heterogeneously catalysed n-propyl propionate synthesis over Amberlyst 46 in a reactive distillation column was feasible. It has to be stressed that no side product (di-n-propyl ether, DPE) was detected in the column.

Due to an excess of 1-propanol and a sufficient amount of catalyst the propionic acid was nearly completed converted in the reactive section ($X_{ProAc} = 96.2\%$), while a large molar fraction of 1-propanol was present in the entire column. N-propyl propionate left the column at the bottom of the column, since it is a high boiling component. A molar fraction of $x_{ProPro} = 0.6$ was achieved in the bottom stream. At the top of the column, a

Table 3. Operating conditions and selected experimental results

	Feed rate [kg/h]	Molar feed ratio POH/ProAc [−]	Reflux ratio [−]	Distillate (m[kg/h]; x_{ProPro}; x_{POH}; x_{ProAc})	Bottom (m[kg/h]; x_{ProPro}; x_{POH}; x_{ProAc})
E1	1.994	2.28	2.24	0.861; 0.027; 0.537; 0.000	1.133; 0.761; 0.167; 0.043
E2	1.990	2.05	1.99	0.798; 0.031; 0.478; 0.000	1.192; 0.797; 0.148; 0.030
E3	1.996	2.44	1.99	0.866; 0.031; 0.557; 0.000	1.130; 0.700; 0.210; 0.023
E4	2.000	2.42	2.46	0.753; 0.020; 0.496; 0.000	1.246; 0.652; 0.321; 0.027
E5	1.997	2.04	2.48	0.677; 0.025; 0.426; 0.000	1.320; 0.698; 0.253; 0.029
E7	1.992	2.06	1.98	0.896; 0.034; 0.535; 0.000	1.096; 0.925; 0.020; 0.037

Table 4. Results of the data reconciliation

Nr.	ϕ	BC	Status
E1	4.7	ok	reconciled
E2	2.8	ok	reconciled
E3	1.5	ok	reconciled
E4	3.5	ok	reconciled
E5	3.5	ok	reconciled
E6	13.0	not fulfilled	–
E7	2.2	ok	reconciled

ternary mixture consisting of 1-propanol, water and n-propyl propionate nearly to the azeotropic 1-propanol/water composition was obtained. The temperature profile shows, that the maximum operating temperature of the catalyst ($T_{max,cat} = 120°C$) was not reached in the column (Figure 4, right).

The liquid phase molar fraction and temperature profile of experiment E7 are illustrated in Figure 5. In comparison to experiment E4, the molar feed ratio of both reactants and also the reflux ratio were kept at lower values while the distillate-to-feed ratio was higher.

A high purity of the ester ($x_{ProPro} = 0.92$) was achieved, while the propionic acid conversion of $X_{ProPro} = 96.5\%$ remains on a same high level compared to E4. Since a higher distillate-to-feed-ratio was realised, 1-propanol and water was stripped out of the lower part of the column. The distillate stream contained 1-propanol, water and low amounts of n-propyl propionate.

The disadvantage of this process configuration comes along with high temperatures of almost 120°C in the lower part of the reactive section (Figure 5 (right)). This has to be taken into consideration for a further process development because an irreversible catalyst deactivation occurs at higher temperatures since the bonding between the sulfonic acid groups and the copolymer matrix destabilise.

VAPOUR PERMEATION

In vapour permeation components are separated by a non-porous membrane due to different sorption and diffusion properties. Consequently the separation is very selective and not

Table 5. Steady state distillate (D) and bottom (B) compositions for E7

	$x_{POH,D}$ [−]	$x_{ProPro,D}$ [−]	$x_{ProAc,D}$ [−]	$x_{H_2O,D}$ [−]	$x_{POH,B}$ [−]	$x_{ProPro,B}$ [−]	$x_{ProAc,B}$ [−]	$x_{H_2O,B}$ [−]
t_1	0.533	0.034	0.000	0.433	0.018	0.927	0.035	0.019
t_2	0.516	0.033	0.000	0.451	0.017	0.928	0.036	0.019
t_3	0.535	0.034	0.000	0.431	0.020	0.925	0.037	0.018

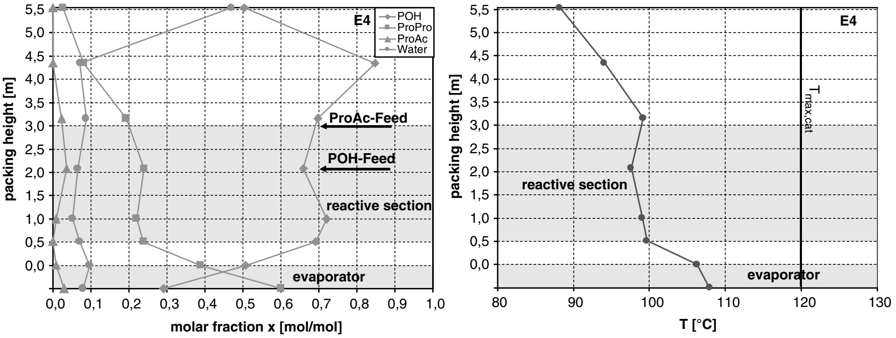

Figure 4. Liquid phase molar fraction (left) and temperature profile of the vapour phase (right) for experiment E4

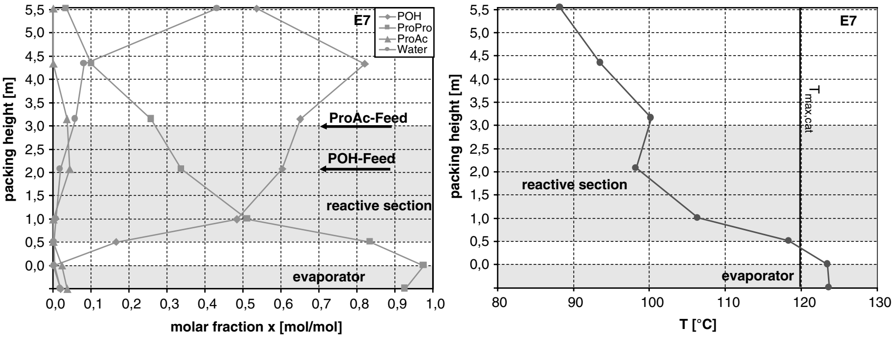

Figure 5. Liquid phase molar fraction (left) and temperature profile of the vapour phase (right) for experiment E7

limited by the vapour-liquid equilibrium. The driving force is generated by lowering the partial pressure of the favourable permeating component on the permeate side by applying a vacuum.

SETUP

A multifunctional lab-scale vapour permeation plant equipped with a rectangular test cell (Figure 6, left) was used in this work for the vapour permeation experiments. To identify the separation characteristic of the polymeric flat sheet membrane Pervap 2201D from Sulzer Chemtech, influences of relevant operational parameters (e.g. feed temperature) on the transmembrane flux and the selectivity were identified.

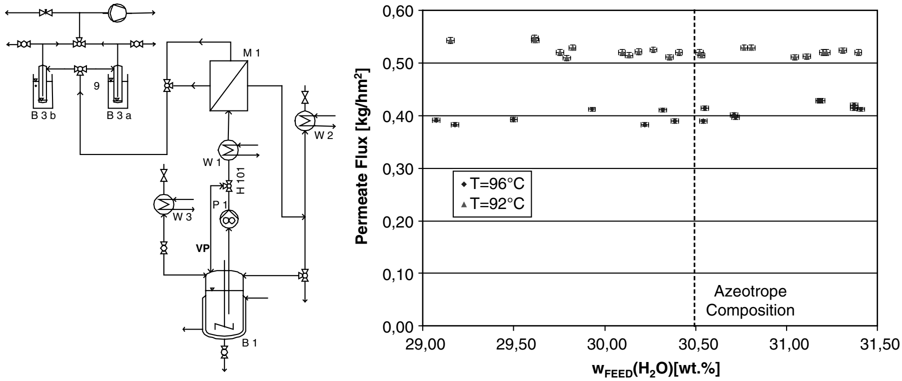

Figure 6. Flowsheet of the lab-scale plant (left), Permeate flux around the azeotropic composition (right)

EXPERIMENTS

Experiments with a binary 1-propanol/water mixture were performed to investigate the separation behaviour of Pervap 2201D ($A_{memb} = 161\ cm^2$) to deplete the obtained distillate stream of the column. All experiments were carried out at a constant permeate pressure of 30 mbar and a vapour feed flow rate of 0.2 kg/h.

In Figure 6 (right) the influence of the feed temperature on the transmembrane flux is illustrated. The feed was superheated at 92°C and 96°C. The membrane was operating around the azeotropic composition independently of the VLE and stable at the chosen operating conditions.

Table 6 summarises the experimental results. The membrane showed moderate permeate fluxes at both temperatures. At the chosen operating conditions, traces of 1-propanol were analysed in the permeate samples. Therefore, the permeance P, being

Table 6. Membrane operating conditions and experimental results

	T = 92°C	T = 96°C
Feed flow rate [kg/h]	0.2	0.2
Permeate pressure [mbar]	30	30
Permeate flux J [kg/m^2 h]	0.52	0.40
P_{H_2O} [kg/m^2 h bar]	1.29	0.84
P_{POH} [kg/m^2 h bar]	1.49E-4	0.98E-4
$\alpha_{H_2O/POH}$ [−]	8650	8550

the quotient of partial permeate flux and driving force in accordance to equation (3)

$$P_i = \frac{J_i}{\Delta DF_i} = \frac{J_i}{(p_{i,\mathrm{Feed}} - p_{i,\mathrm{Permeate}})} \tag{3}$$

was low for 1-propanol in the investigated range of the feed composition. It can be stated that the membrane was nearly 100% selective towards water.

CONCLUSIONS

The operation of a plant consisting of coupled reactive distillation and vapour permeation is very complex. Therefore the independently operated units were experimentally investigated in order to prove their feasibility for the n-propyl propionate synthesis. The experiments performed in a stand-alone RD column showed, that the almost pure ester was produced as bottom product whereas 1-propanol and water with low amounts of n-propyl propionate appeared in the distillate. The influence of different operating conditions was investigated. High acid conversions and product purities could be achieved. The quality of the experimental results was enhanced by the application of a data reconciliation.

Vapour permeation experiments with the binary alcohol/water mixture at its azeotropic composition proved the suitability of the used polymeric membrane Pervap 2201D. The membrane was stable at the operating conditions and showed moderate fluxes.

The future works will focus on the integration of reactive distillation and vapour permeation as well as on modelling of the complex behaviour of the integrated unit.

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