

TRANSESTERIFICATION PROCESSES BY COMBINATION OF REACTIVE DISTILLATION AND PERVAPORATION

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ABSTRACT

The development of a reactive distillation process for the production of n-butyl acetate by transesterification of methyl acetate with n-butanol is presented. Thermodynamic aspects of the quaternary system n-butyl acetate – n-butanol – methyl acetate – methanol are discussed and UNIQUAC interaction parameters derived using the Dortmund Data Bank (DDB) are given. The reaction kinetics of the heterogeneously by a strongly acidic ion-exchange resin (Amberlyst 15) catalyzed reaction has been investigated and the kinetic constants for a pseudohomogeneous kinetic model are presented. Pervaporation experiments using a Pervap 2250-60 membrane have been performed for the separation of the methanol - methyl acetate binary mixture which forms the distillate stream of the reactive distillation column. Measurements concerning the separation efficiency of Katapak[®]-SP have been conducted. Reactive distillation experiments have been performed using the structured catalytic packings Katapak[®]-S and Katapak[®]-SP. Important operating conditions (reflux ratio, total feed rate) have been varied experimentally. The experimental results are presented in comparison with simulation results. An equilibrium stage model for the modeling of the distillation is capable of describing the composition profiles quantitatively. The simulation has been used subsequently to determine the influence of important operating and design variables. Finally a new process, combining reactive distillation with pervaporation, has been developed and investigated by means of simulation studies. It has been shown that the combination of reactive distillation with pervaporation is favorable since conversions close to 100% can be obtained with a reasonable size of the reactive section.

INTRODUCTION

Due to its high potential for process intensification, reactive distillation has gained increasing interest in the last years not only in industrial but also in academic research. Especially for equilibrium limited reactions and consecutive reactions, reactive distillation may lead to higher conversions and selectivities and can therefore reduce capital and investment costs significantly. The direct removal of the products from the reactive section of the column by distillation results in higher conversions (100% in the ideal case) and higher selectivities. Although invented in 1921 [1], the industrial application of reactive distillation took place in the 1980s [2].

Reactive distillation has been applied to different etherifications, esterifications and ester hydrolysis reactions in the past. Mainly the synthesis and hydrolysis of methyl acetate has been investigated extensively and now serves as a model system for reactive distillation processes [3,4].

Like esterifications, transesterifications are typical equilibrium limited reactions and in contrast to the different esterifications and etherifications only little information about transesterification reactions by reactive distillation can be found in literature. Especially for the reaction considered for this investigation, the transesterification of n-butanol with methyl acetate forming methanol and n-butyl acetate (Equation 1), no literature data are available.



Transesterifications usually have equilibrium constants close to unity and a low reaction rate. Hence reactive distillation might be a promising process alternative. A search in the CAS database [5] indicated that no information is available about the considered system in the open literature.

n-Butyl acetate is an important solvent in chemical industry. Primarily it is used in paint and coating manufacture and the lacquer industry. Methyl acetate is a by-product of the poly-(vinyl)-alcohol production and has to be converted to methanol which is a feedstock of the poly-(vinyl)-alcohol production.

The transesterification of methyl acetate with n-butanol forming n-butyl acetate and methanol was not only chosen due to economic interests but also to check whether reactive distillation can be applied successfully to a system with a low reaction rate, an equilibrium constant close to unity and a complex phase equilibrium behavior. Due to two binary pressure maximum azeotropes (methanol – methyl acetate, n-butanol – n-butyl acetate), a conventional process where reaction and separation occur subsequently, would lead to a relatively complex separation train downstream the reactor. A low reaction rate and an equilibrium constant close to unity lead to a large number of reactive stages necessary in a reactive distillation process. Therefore the combination of reactive distillation with other unit operations should be considered. Pervaporation or steam permeation are suitable unit operations for the separation of azeotropic mixtures. Pervaporation denotes a membrane process where a liquid feed is divided into a liquid retentate and a vaporous permeate, which is maintained by evacuation. The selectivity is governed by the transport rate through the membrane as a result of different solubilities and diffusivities of the components. Solubilities and

diffusivities are difficult to predict and therefore pragmatic models are often applied to describe the separation performance of the membrane.

The aim of this paper is to present the development of a kinetically controlled reactive distillation process and to show possible combinations of other unit operations with reactive distillation. The reaction is carried out in a reactive distillation column combined with a prereactor. Subsequently pervaporation is used to separate the methyl acetate – methanol binary mixture which is obtained as distillate. While methyl acetate is recycled into the reactive distillation column, methanol can be obtained as product in the permeate.

Designing a reactive distillation process requires detailed information about the pure component properties as well as data about the phase and the chemical equilibrium. Furthermore data about the reaction kinetics are necessary. Pilot-plant experiments are essential during the development procedure in order to ensure the reliability of the process simulation so that simulation can be used to identify the role of important design factors like size and location of the reactive section and for process optimization.

Heterogeneously catalyzed reactive distillation offers advantages over the homogeneously, e.g. by sulfuric acid, catalyzed alternative. The size of the reactive section can be chosen independently from thermodynamic constraints and corrosion problems can be minimized. The immobilization of the heterogeneous catalyst inside the reactive section of the column can be achieved by structured packings like Katapak[®]-S (Sulzer Chemtech) or Katapak[®]-SP (type SP 11, Sulzer Chemtech) which are used in this investigation [6]. Katapak[®]-S and Katapak[®]-SP are made of wire-mesh sheets. Any catalyst with the size between 0.5 and 2 mm can be stored between the sheets of the packing. Katapak[®]-S offers a higher NTSM (number of theoretical stages per meter) value but has a lower amount of catalyst per meter packing in comparison with Katapak[®]-SP. Katapak[®]-S has already been used for many esterifications, etherifications and ester hydrolysis reactions [3]. Up to now, only little information is available about Katapak[®]-SP. One of the aims of this paper is to determine whether a higher amount of catalyst per section (Katapak[®]-SP) or a higher amount of theoretical stages per meter (Katapak[®]-S) is more advantageous for reactive distillation processes. In this investigation the strongly acidic ion-exchange resin Amberlyst 15 (Rohm & Haas) was used as a catalyst. This catalyst has also been applied by Pöpken et al. [3] for the methyl acetate synthesis.

THERMODYNAMIC ASPECTS

Information about the vapor-liquid equilibrium (VLE) and the equilibrium constant of the reaction play a major role in the development of reactive distillation processes. The activity coefficients γ_i are necessary for taking into account the liquid phase non-idealities. In this work the UNIQUAC equation [7] was used for the calculation of γ_i , which are not only used for the calculation of the phase equilibria but also for the accurate description of chemical equilibrium and the reaction kinetics. Polynomial temperature dependent parameters were used according to Equation 2 to be able to describe the composition and temperature dependency of the excess Gibbs energy (resp. the activity coefficient).

$$\Delta u_{ij} = a_{ij} + b_{ij}T + c_{ij}T^2 \quad (2)$$

The r and q values (Table 1) were taken from the Dortmund Data Bank (DDB), Version 2002, which was kindly placed to our disposal by the DDBST GmbH Oldenburg, Germany [8].

Table 1 UNIQUAC r_i and q_i values

component	r_i	q_i
methyl acetate	2.8042	2.5760
n-butanol	3.4543	3.0520
n-butyl acetate	4.8274	4.1960
methanol	1.4311	1.4320

Interaction parameters were fitted simultaneously to different kind of phase equilibrium data and excess properties which were taken from the DDB (VLE, azeotropic data, activity coefficients at infinite dilution (γ^∞), heats of mixing (h^E)). In order to account for the excess Gibbs energy only, the temperature independent parameters of the Antoine equation were adjusted to the experimental pure component vapor pressure given by the author during the parameter fitting procedure. The resulting parameters are given in Table 2.

Table 2 UNIQUAC interaction parameters used for the calculation of activity coefficients

component 1	component 2	i	j	a_{ij} (K)	b_{ij} (-)	c_{ij} (K ⁻¹)
methyl acetate	methanol	1	2	326.2	0.725	-2.365×10^{-3}
		2	1	62.97	-0.720	1.17×10^{-3}
n-butanol	methyl acetate	1	2	-21.08	0.556	0.0
		2	1	339.3	-1.174	0.0
n-butanol	methanol	1	2	600.3	-4.047	6.44×10^{-3}
		2	1	-636.2	4.550	-7.25×10^{-3}
n-butyl acetate	methanol	1	2	492.7	-0.083	0.0
		2	1	9.396	-0.337	0.0
n-butanol	n-butyl acetate	1	2	-48.26	0.200	-4.54×10^{-4}
		2	1	260.1	-0.499	2.12×10^{-4}
n-butyl acetate	methyl acetate	1	2	-1340	4.297	0.0
		2	1	937.1	-2.963	0.0

Because of the relatively low pressure, vapor-phase non-idealities are neglected during the VLE calculation. An overview of the azeotropes present in the system is given in Table 3. The calculated azeotropes are compared with data from literature. The azeotropes listed are present under non-reactive conditions.

Table 3 Non-reactive azeotropes present at 1 atm

System	Temp. (K)	Azeotropic composition (calculated)	Azeotropic composition (from 10)	Type
n-butanol – n-butyl acetate	390.05	y (n-butanol) = 0.8069	y (n-butanol) = 0.729 – 0.795	hom. P max.
methanol – methyl acetate	327.49	y (methanol) = 0.3455	y (methanol) = 0.32 – 0.352	hom. P max.

Azeotropes between reactants and products can be circumvented by reaction. According to the reactive residue curve map which is given in Figure 1, no reactive azeotropes are present in the system. Reactive residue curve maps which are based upon transformed coordinates can be used for an initial process design [11,12].

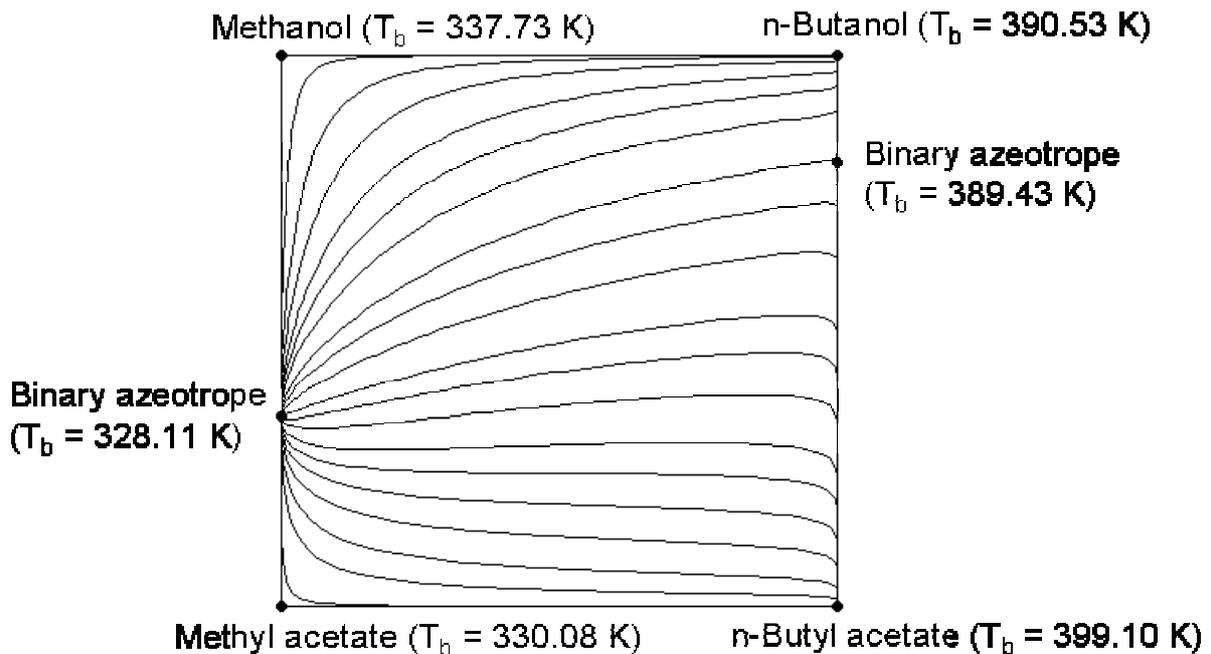


Figure 1. Reactive Residue Curve Map

The equilibrium constant K_a is given by

$$K_a = \prod a_i^{v_i} = \prod x_i^{v_i} \times \prod \gamma_i^{v_i} \quad (3)$$

The equilibrium constant is related to the standard Gibbs energy of reaction Δg_r^0 by

$$\ln(K_a) = -\Delta g_r^0 / RT^0 \quad (4)$$

The temperature dependency of the equilibrium constant is given by the van't Hoff equation

$$\ln(K_a) = \ln K_a(T^0) - \frac{\Delta h_r^0}{R} \left(\frac{1}{T} - \frac{1}{T^0} \right) \quad (5)$$

Data for the standard Gibbs energy of reaction and the standard enthalpy of reaction can be calculated from the standard Gibbs energy of formation and the standard enthalpy of formation. Temperature dependencies of the enthalpies can be taken into account with the help of heat capacities, which are also stored in the DDB. The reaction is slightly exothermic and therefore the equilibrium constant K_a decreases with increasing temperature. The equimolar equilibrium conversion at 333.15 K at 1 bar is 47.23%. The equilibrium constant in the temperature interval between 333.15 K and 393.15 K at 1 bar can then be written as

$$\ln K_a = \frac{326.1}{T} - 1.097 \quad (6)$$

EXPERIMENTAL SECTION

Chemicals. The chemicals used for the reaction kinetic experiments were of analytical grade (99.8%). The chemicals were dried over molecular sieve prior to use. For the reactive distillation experiments the chemicals were of reaction grade (99.5%) and were used without further purification. Methyl acetate was supplied by Riedel-deHaen, n-butanol was supplied by BASF, Methanol was supplied by Scharlau and n-butyl acetate was supplied by Aldrich. The purity of the chemicals was verified by gas chromatography.

Analytcs. All samples were analyzed by gas chromatography using a HP 6890 with TCD (He as carrier gas at 1.682 bar; HP-Innowax 30 m × 0.032 mm; split 10:1; temperature program ; 313 K hold for 4 min, heat at 338 K min⁻¹ to 453 K hold for 1.5 min; typical retention times : 3.3 min for methyl acetate, 4 min for methanol, 6 min for n-butyl acetate and 6.7 min for n-butanol).

REACTION KINETICS

Besides reliable thermodynamic data, accurate information about the kinetics are most important for a successful design of reactive distillation processes. Although most reactive distillation modeling and simulation studies consider the reaction to be infinitely fast and therefore assume chemical equilibrium on every ideal reactive stage, it has recently been shown for the methyl acetate synthesis and hydrolysis [3] that the knowledge of the reaction kinetics is of great importance for the modeling of reactive distillation processes. For the transesterification investigated in this work it can be assumed that the reaction is significantly slower and the influence of the reaction kinetics will still be more important.

To the best of our knowledge, information about the reaction kinetics of the transesterification of methyl acetate with n-butanol using the strongly acidic ion-exchange resin Amberlyst 15 as a catalyst, have not been published.

The experiments were conducted in a thermostated stirred tank glass reactor with a volume of 500 cm³. The temperature of the heating jacket was kept constant within ± 0.1 K. The stirrer was plate-type and the speed was variable. To improve mixing, a baffle was installed. Furthermore a reflux condenser was installed in order to avoid any loss of volatile components. Liquid samples of about 1 cm³ were taken using a syringe and weighed (accuracy of the balance ± 0.001 g).

Prior to use, Amberlyst 15 was washed several times with water until the supernatant liquid was colorless. The catalyst was dried at 353.15 K under vacuum until the mass remained constant (usually two days). The ion-exchange capacity of Amberlyst 15 has been determined earlier [13].

Before the kinetic experiment was started both reactants were brought to reaction temperature in separate vessels. The catalyst was added to one of the reactants about 5 minutes before the start of the experiment. When the desired temperature was reached the reactor was filled with both reactants. Immediately afterwards the stirrer and the time measurement started and samples were drawn according to a measurement program. During one experiment between 15 and 20 samples were taken. The samples were cooled rapidly to 277.15 K to avoid any further reaction and analyzed by gas chromatography. In none of the runs side products have been detected.

In order to determine the effect of the external mass transfer, the stirrer speed was varied between 100 and 600 rpm. Above 200 rpm no influence of the stirrer speed was detected. Therefore all further runs were performed with a stirrer speed of 400 rpm. These results are in a good agreement with those found by Pöpken et al. [13] for the methyl acetate synthesis. These authors also proofed the absence of internal mass-transfer for the methyl acetate synthesis. Also Xu and Chuang [14] stated that internal diffusion is insignificant for the esterification of acetic acid with methanol catalyzed by Amberlyst 15. Due to the fact that Amberlyst 15 is composed of very small gel-type microspheres with large macropores [15], internal mass-transfer can also be excluded for the transesterification considered in this work.

Measurements were performed between 313.15 K and 325.15 K. Besides the temperature, the catalyst and the initial reactant ratio was varied. The forward and backward reaction were studied. Kinetic constants for both directions can be obtained by the fitting procedure from each run, no matter whether the reaction of n-butanol with methyl acetate or the reaction of methanol with n-butyl acetate was studied. Hence the data presented here are valid for both directions.

Both, pseudohomogeneous and adsorption based models have been used to describe the heterogeneously by ion-exchange resins catalyzed esterification reactions. It has been shown for esterification and etherification reactions that the presence of water has an important influence on the kinetics since it is preferentially sorbed by the resin due to its small molecular size and high polarity. The components present in this investigation have nearly the same molecular size and polarity. Therefore it can be assumed that the components present have similar affinities to the resin and sorption effects can therefore be neglected and a pseudohomogeneous model should be sufficient.

Transesterification reactions are known to be reversible reactions of second order. A pseudohomogeneous kinetic model can then be written as

$$r = \frac{1}{m_{cat}} \frac{1}{v_i} \frac{dn_i}{dt} = k_1 a_{BuOH} a_{MeOAc} - k_{-1} a_{MeOH} a_{BuOAc} \quad (7)$$

Activities are used instead of concentrations or mole fractions. This leads to a more consistent and accurate description [13]. The kinetic constants k_1 and k_{-1} can be fitted to the experimental data by numerically integrating the kinetic equations using a fourth-order Runge-Kutta method and minimizing the mean squared deviation of the calculated and the measured concentrations.

The temperature dependency of the rate constant is expressed by the Arrhenius' law :

$$k_i = k_i^0 \exp\left(\frac{-E_{A,i}}{RT}\right) \quad (8)$$

Four adjustable parameters (k_1^0 , k_{-1}^0 , $E_{A,1}$, $E_{A,-1}$) have to be fitted to describe the concentration and temperature dependency of the reversible reaction. The values are given in Table 4. All values for the activation energy given in this work are apparent factors, i.e. they should not be interpreted on a molecular level.

Table 4 Kinetic parameters for the pseudohomogeneous kinetic model

reaction	i	k_i [mol g ⁻¹ s ⁻¹]	$E_{A,i}$ [kJ mol ⁻¹]
esterification	1	105.74	44.20
hydrolysis	-1	84.22	42.81

The values resulted from the overall fit of the four variables (k_1^0 , k_{-1}^0 , $E_{A,1}$, $E_{A,-1}$) to all experimental data are shown in the Arrhenius diagram (Figure 2). As can be seen from Figure 3 the assumption of a linear relationship between the reaction rate and the catalyst mass is valid. The kinetic constants given in Table 4 are incorporated into the process simulator.

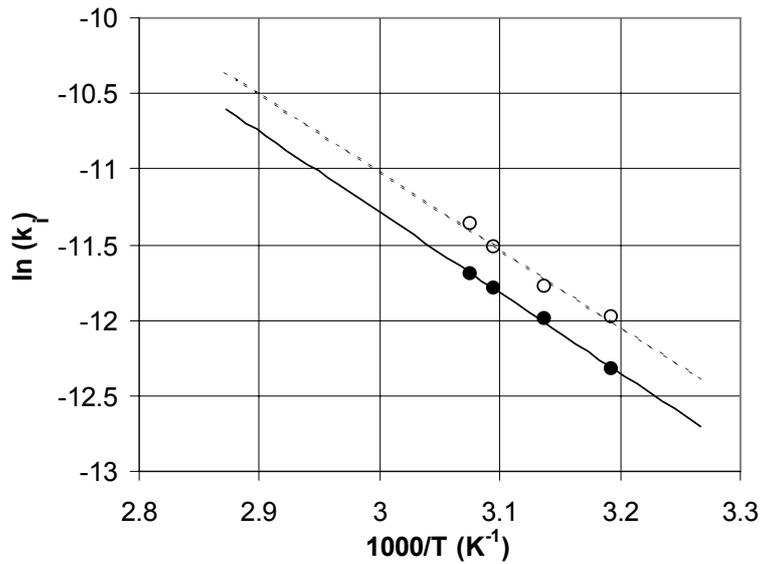


Figure 2. Arrhenius diagram of the rate constants for the reaction of methyl acetate with *n*-butanol k_1 (●) and the backward reaction k_{-1} (○) of the heterogeneously catalyzed reaction. The lines represent the results of the overall fit.

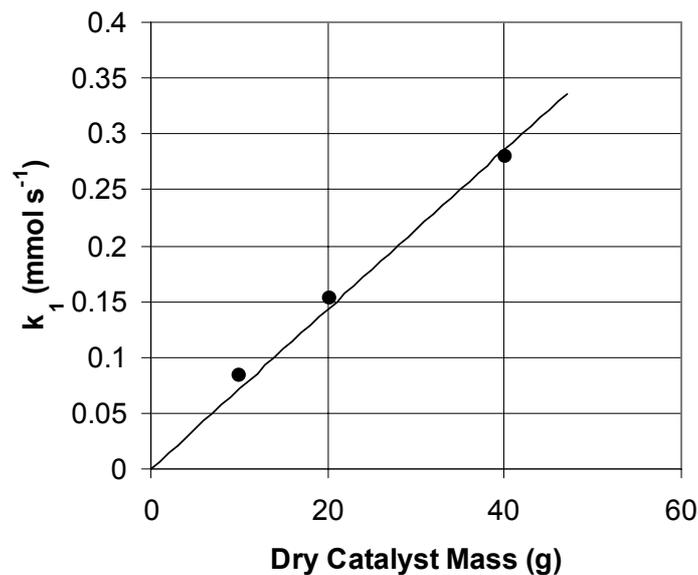


Figure 3. Rate constants for the forward reaction k_1 (●) at 323 K versus catalyst mass. The line presents the overall fit.

PERVAPORATION

Pervaporation experiments were performed using a stirred semi-batch setup. In order to achieve quasi-stationary conditions a thermostated vessel ($\pm 0.1 \text{ K}$) with a high liquid holdup (appr. 5 dm^3) was used as a feed buffer tank. A circular flat sheet membrane in a membrane module made by GKSS with an effective membrane area of 0.01 m^2 was

applied for this investigation. The feed enters the membrane module through a small annular gap and the retentate leaves the membrane module in the center of the membrane. The membrane is fixed in a perforated plate. A gear pump (Gather Industries) with a variable flow is used as a feed pump. The permeate is collected in a cooling trap operated at 77 K (liquid nitrogen). The retentate is refluxed into the feed buffer tank. Vacuum at the permeate side was maintained at < 7 mbar within ± 1 mbar by an Vacuubrand model vacuum pump. Before each run membranes were left overnight in a closed flask, placed in a constant temperature bath containing a liquid mixture of methanol – methyl acetate. After starting the pervaporation runs the membrane is allowed to reach equilibrium for about 3 hours. After that samples were drawn every 30 minutes and the amount of permeate was weighed using a balance (accuracy ± 0.01 g) until stationarity is obtained (usually 2 hours). Samples from the permeate and the feed stream were analyzed by gas chromatography.

Pervaporation results for the Pervap 2250-60 membrane (Sulzer Chemtech) are shown in Figure 4. The results indicate that it is possible to separate methyl acetate – methanol mixtures by pervaporation and that the considered membrane leads to an enrichment of methanol in the permeate. This is advantageous since high amounts of methyl acetate can be expected in the distillate stream leaving the reactive distillation column and therefore a smaller membrane area will be needed to separate methanol from methyl acetate. But it can be seen that the selectivity of the membrane used is not sufficient for the combination with reactive distillation. Therefore ongoing research focuses on the investigation of membranes with higher selectivities like the cuprophane membrane which already has been applied for the separation of the methyl acetate – methanol mixture [16].

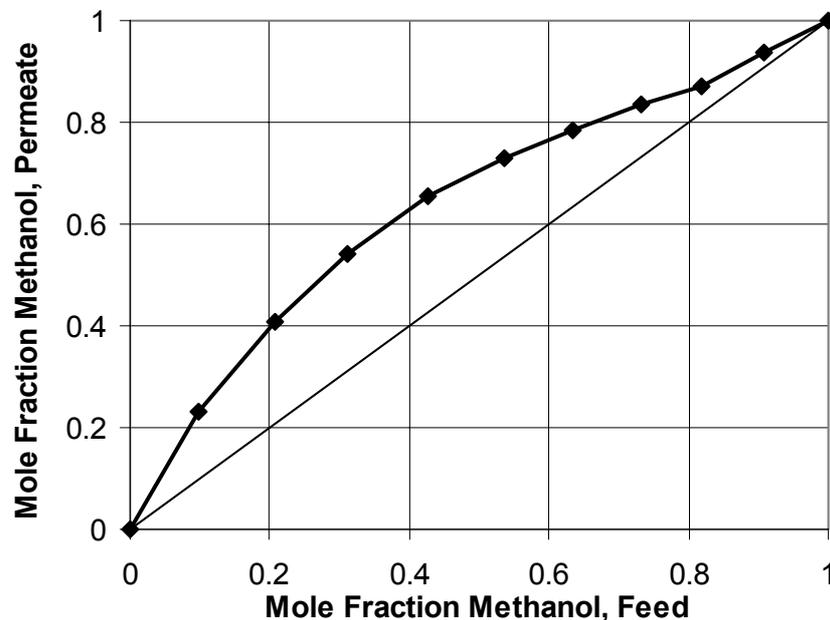


Figure 4. Pervaporation result for Pervap 2250-60.

SEPARATION EFFICIENCY OF THE PACKINGS

The separation efficiency of the Katapak[®]-S elements used in this work has been determined earlier [3]. With the test system water – acetic acid a NTSM value of about 4 m⁻¹ was obtained. Since no data for the separation efficiency of the laboratory version of Katapak[®]-SP were available in literature, the NTSM value was determined during this investigation with a column setup consisting of 1 m of Katapak[®]-SP. Since no water is present in the system, the detrimental influence of water on the separation efficiency can be neglected. For the purpose of comparison the binary system water – acetic acid was used as a test system. The NTSM value was calculated from the measured concentrations using the known VLE of the system [8]. As can be seen from Figure 5 the NTSM value of about 2 m⁻¹ was obtained. This results are in good agreement with those for the 250 mm diameter packing (test system : chlorobenzene - ethylbenzene) [6]. For the small range of liquid loads (F-Factors [9] between 0.1 Pa^{0.5} and 1.5 Pa^{0.5}) used in this investigation, the separation efficiency can be considered independent from the liquid load.

For the simulation a NTSM value of 4 m⁻¹ was used for the Katapak[®]-S packings whereas a value of 2 m⁻¹ was set for the Katapak[®]-SP packing. For the non-reactive Sulzer-BX packings a NTSM value of 5 m⁻¹ was set for simulation during this investigation.

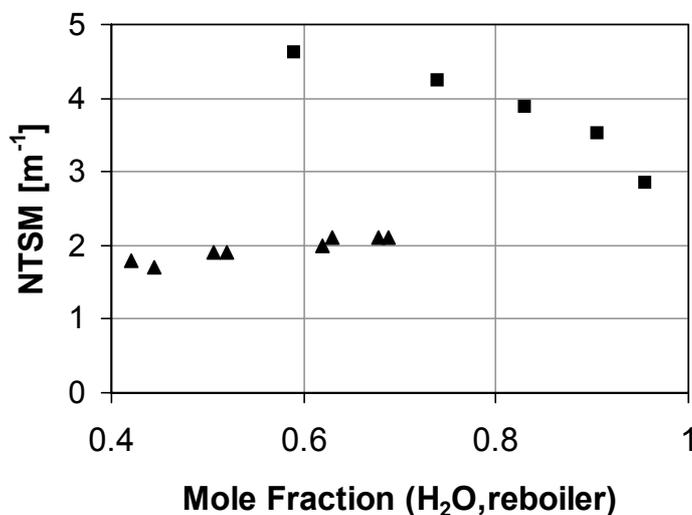


Figure 5. Separation efficiency of the packings used in this investigation (Katapak[®]-S: ■ taken from [3]; Katapak[®]-SP: ▲)

REACTIVE DISTILLATION EXPERIMENTS

The experiments in the pilot-plant scale were performed in a glass column supplied by QVF (QVF Engineering) with an inner diameter of 50 mm. A vessel with a low liquid holdup (appr. 1 dm³) was applied as a reboiler in order to achieve stationarity in a reasonable period of time. In the reboiler the liquid was heated electrically by rod-

shaped quartz heaters (Vogelsberger Quarzglasstechnik). The reboiler duty was controlled by a transformer and connected with a digital multimeter (Votcraft M-3860M) to within $\pm 1\%$.

The reactive section consisted of Katapak[®]-S or of Katapak[®]-SP packings whereas the non-reactive sections contained Sulzer-BX packings. Each column section has a height of 1.2 m and an effective packing height of 1 m. Except the flanges and the reboiler the column was insulated by a vacuum jacket. The flanges and the reboiler were insulated by aluminum foil and mineral wool. Nevertheless the heat loss of the column was determined. A linear relationship between the heat loss and the temperature inside the column has been shown elsewhere [3]. The following equations can be used to describe the heat loss :

$$\dot{Q}_{loss, reboiler} = 3.8 WK^{-1} \Delta T \quad (9)$$

$$\dot{Q}_{loss, per\ section} = 0.39 WK^{-1} \Delta T \quad (10)$$

The reflux ratio was set by a reflux splitter located directly below the condenser. While the reboiler duty and the reflux ratio were set to a fixed value, the liquid level in the reboiler was controlled by an outlet valve which was connected to a light-barrier system. Membrane pumps (Gamma 4-RS, ProMinent) were used as feed pumps. All feed streams were measured by determining the mass flow using balances (accuracy ± 1 g). The column was controlled by a process control system based upon Opto Boards (Optoware) which were connected to a PC (WinNT-workstation). The temperatures were measured using Pt-100 thermometers with an accuracy of ± 0.1 K. Thermometers were installed at the lower end of each column section (except the feed position), in the reboiler, in the vapor coming up into the condenser and in the liquid coming down from the condenser. The top and bottom pressure as well as the pressure drop were measured using pressure transducers (Bosch, accuracy $\pm 0.1\%$). All data were recorded by the process control system and stored in a computer file.

At the lower end of each column section, in the reboiler and from the distillate stream, samples were drawn using a syringe and immediately cooled to 277 K and analyzed by gas chromatography. Below the reactive section, the liquid load was determined by recording the time needed to collect a specified amount of liquid (40 cm^3) in a graduated vessel inside the column.

SIMULATION

All simulations were carried out with the steady state model RADFRAC from the process simulator Aspen-Plus (Version 10.2). The model is based upon a rigorous equilibrium stage model for solving the MESH equations [17]. Stages are numbered from the top to the bottom with the condenser being the first stage and the reboiler being stage N. This results to a total number of 28 stages for the setup with Katapak[®]-S packings and 20 stages for the column equipped with Katapak[®]-SP (Figure 6).

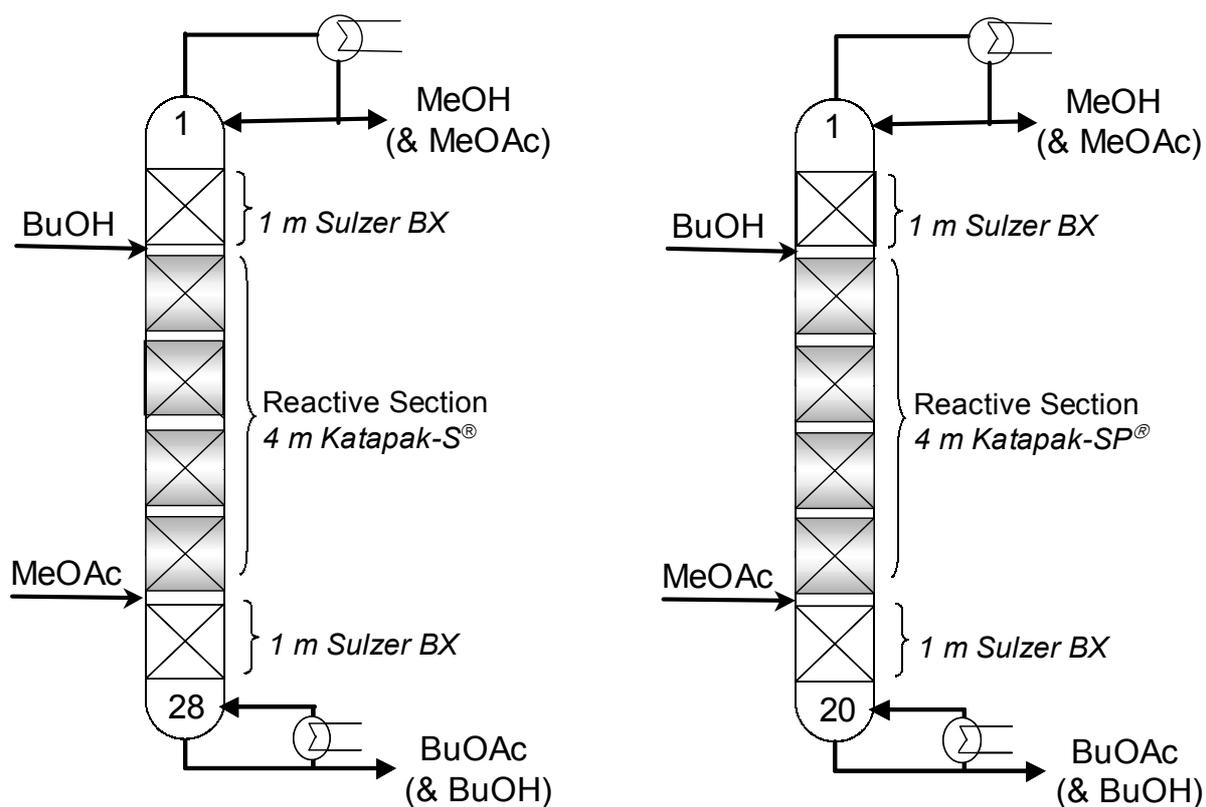


Figure 6. Scheme of the setups used in this work.

Besides the UNIQUAC interaction parameters, data about the column heat loss and the reaction kinetics are incorporated into the process simulator. For the modeling of the prereactor, an equilibrium reactor model operated at 323.15 K and 1 bar was used. The SEP model from Aspen-Plus was used for the pervaporation calculations.

EXPERIMENTAL RESULTS FOR THE REACTIVE DISTILLATION EXPERIMENTS

n-Butyl acetate is the high boiling product and methanol the light boiling product in the reactive system. Due to the existence of two binary azeotropes and the considerably slow reaction rate it can be expected that methyl acetate is present in the distillate and n-butanol is present in the bottom stream. In order to ensure that the process simulation proposed in the previous section is capable of describing the column profiles quantitatively experiments were performed and compared with simulation results. A typical composition profile for the column equipped with Katapak[®]-S and Katapak[®]-SP is shown in Figure 7.

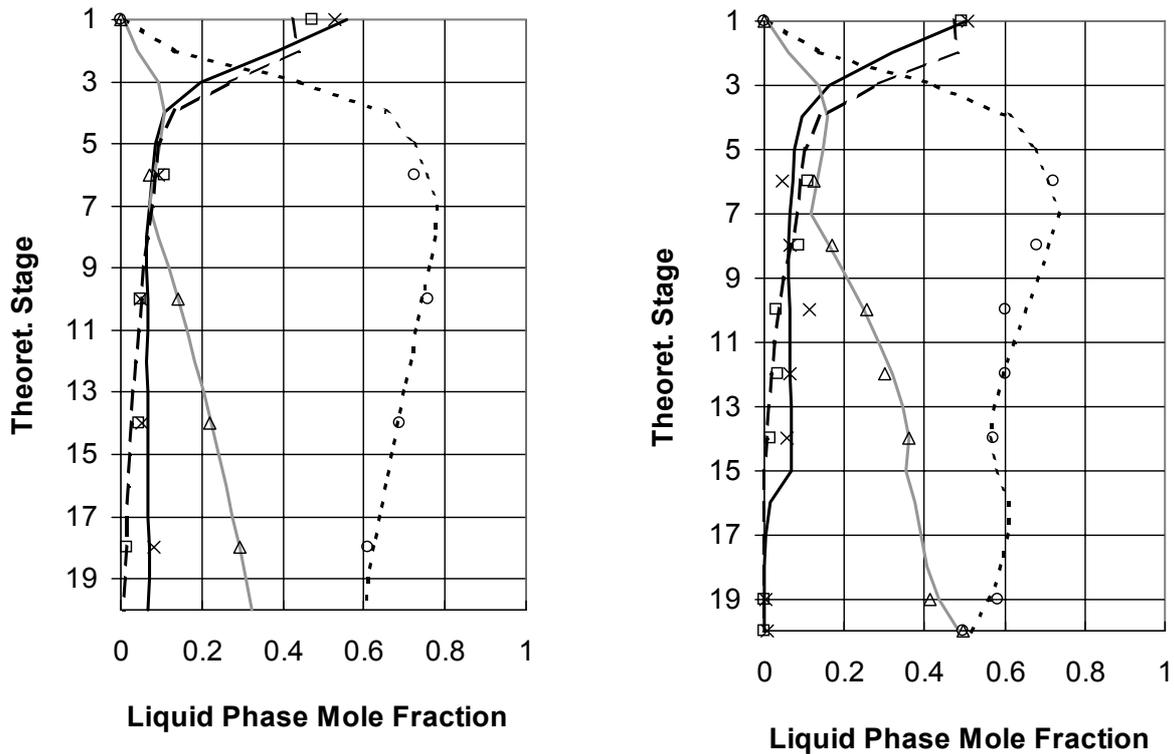


Figure 7. Liquid phase composition profile for the setup with Katapak[®]-S (left hand side) and Katapak[®]-SP (right hand side). Experimental data (BuOAc: \square ; MeOH: \square ; MeOAc: \times ; BuOH: \circ) are compared with simulation results (BuOAc: gray; BuOH: - - - -; MeOH: - - - -; MeOAc: —).

It can be seen that the experimental data are in a good agreement with the simulation results. Please note that these results were obtained without fitting any further constants to data from the pilot-plant experiments. Figures 8 and 9 show the influence of the reflux ratio and the total feed rate on the conversion. The agreement between experimental data and simulation results is within experimental error. Deviations between simulation results and experimental data are mainly caused by differences in the operation conditions (e.g. D:F-ratio) since it was not possible to vary one operation condition and let the others exactly unchanged. Variation of the reflux ratio, for example, also leads to a variation of the reboiler duty when a constant D:F-ratio should be kept. Since small deviations in the reboiler duty might have a large influence on the D:F-ratio, the D:F-ratio varies from one experiment to the other.

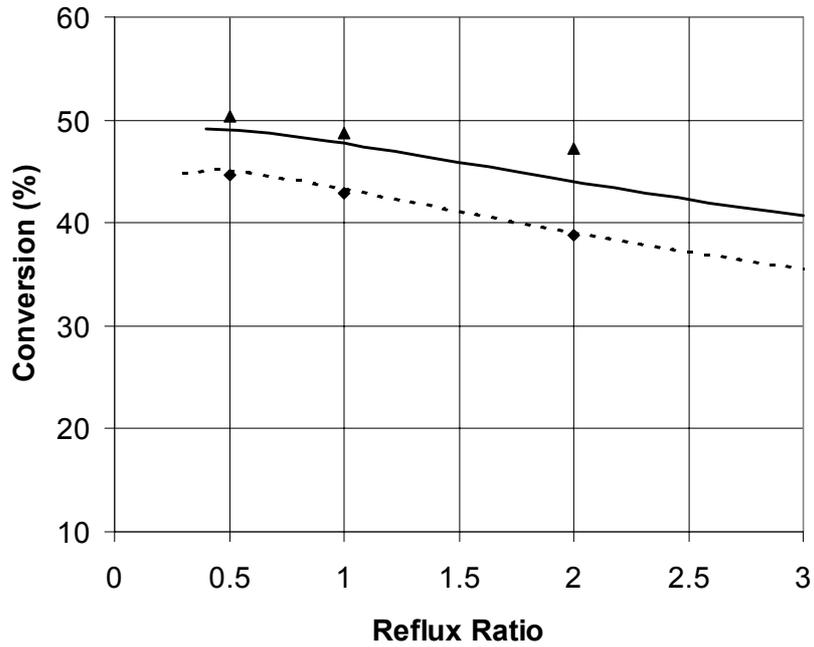


Figure 8. Influence of the reflux ratio on the conversion. Experimental data (Katapak®-SP: ▲; Katapak®-S: ◆) and simulation results (Katapak®-SP: —; Katapak®-S: — —; $\dot{F}_{MeOAc} = \dot{F}_{BuOH} = 0.02 \text{ kmol h}^{-1}$; $D:F = 0.51$; $P = 1 \text{ bar}$).

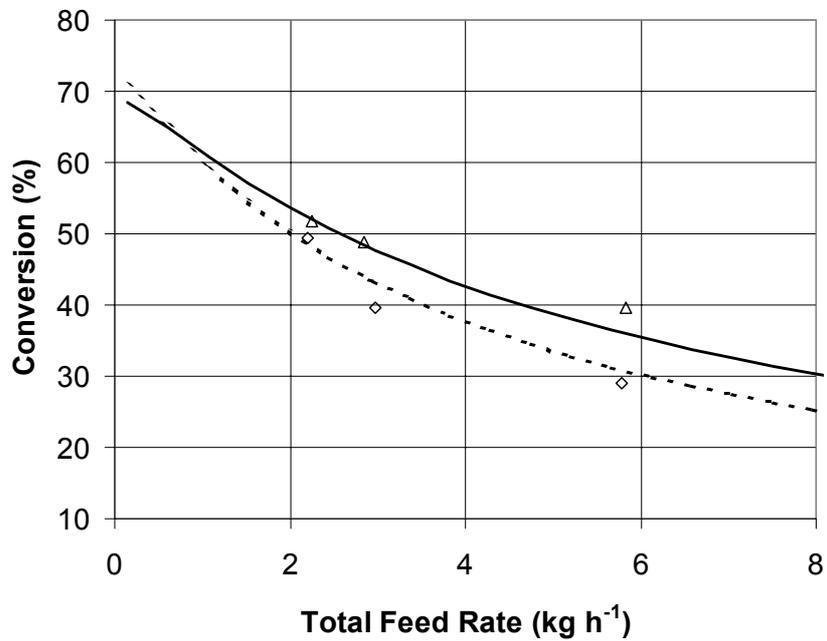


Figure 9. Influence of the total feed rate on the conversion. Experimental data (Katapak®-SP: ▲; Katapak®-S: ◆) and simulation results (Katapak®-SP: —; Katapak®-S: — —; $D:F = 0.51$; $v = 1$; $P = 1 \text{ bar}$).

MODELING

It has been shown in the previous section that reactive distillation should be a favorable process alternative since conversions beyond equilibrium conversion can be obtained. But the conversions achieved with the setups presented here is not sophisticated since further separation trains are necessary. Therefore further options have to be evaluated using the simulation which is an appropriate tool for process evaluation as shown before. For the purpose of general validity all further calculations were conducted with the assumption of a negligible column heat loss.

One important option to increase conversion in a reactive distillation process is to elevate the column pressure and therefore to achieve higher temperatures (higher reaction rates) in the reactive section. The influence of the pressure on the conversion for the Katapak[®]-SP setup (Figure 6) is shown in Figure 10 and it can be seen that higher conversions can be obtained. But it should be mentioned that the temperature in the reactive section rises to values higher than 393 K which is the maximum operating condition of the catalyst presently used at pressures above 1.8 bar.

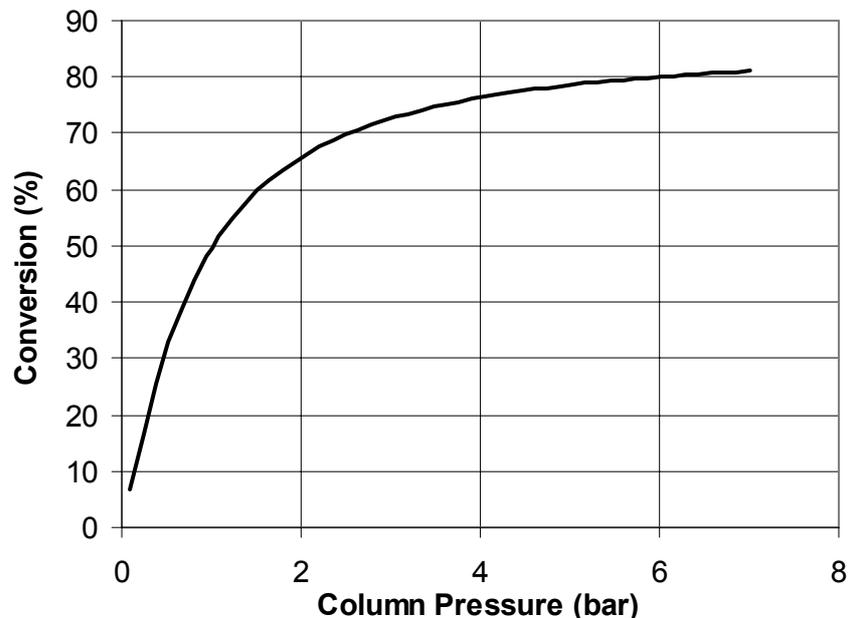


Figure 10. Influence of the pressure on the column performance
($\dot{F}_{MeOAc} = \dot{F}_{BuOH} = 0.02 \text{ kmol h}^{-1}$; $D:F = 0.51$; $v = 1$,
setup according to Figure 6 with Katapak[®]-SP)

Figure 11 shows the influence of amount of catalyst per stage for a 50 mm diameter column and the number of reactive stages on the conversion. It can be concluded that both, separation efficiency and a sufficient amount of catalyst per reactive stage is necessary to obtain high conversions. Furthermore it can be seen that even for a high number of stages and a large amount of catalyst (Katapak[®]-S has 0.0375 kg catalyst per stage and Katapak[®]-SP has 0.105 kg catalyst per stage) it is not possible to achieve conversions of nearly 100%. Due to chemical equilibrium which can be obtained when high amounts of catalyst are available, a certain amount of non-reacted n-butanol is present at the last reactive stage. This leads to a decrease in conversion because n-

butanol is enriched in the non-reactive part below the methyl acetate feed location. Otherwise it is not possible to avoid this non-reactive section since a methyl acetate stripping is necessary to avoid that methyl acetate is present in the bottom stream.

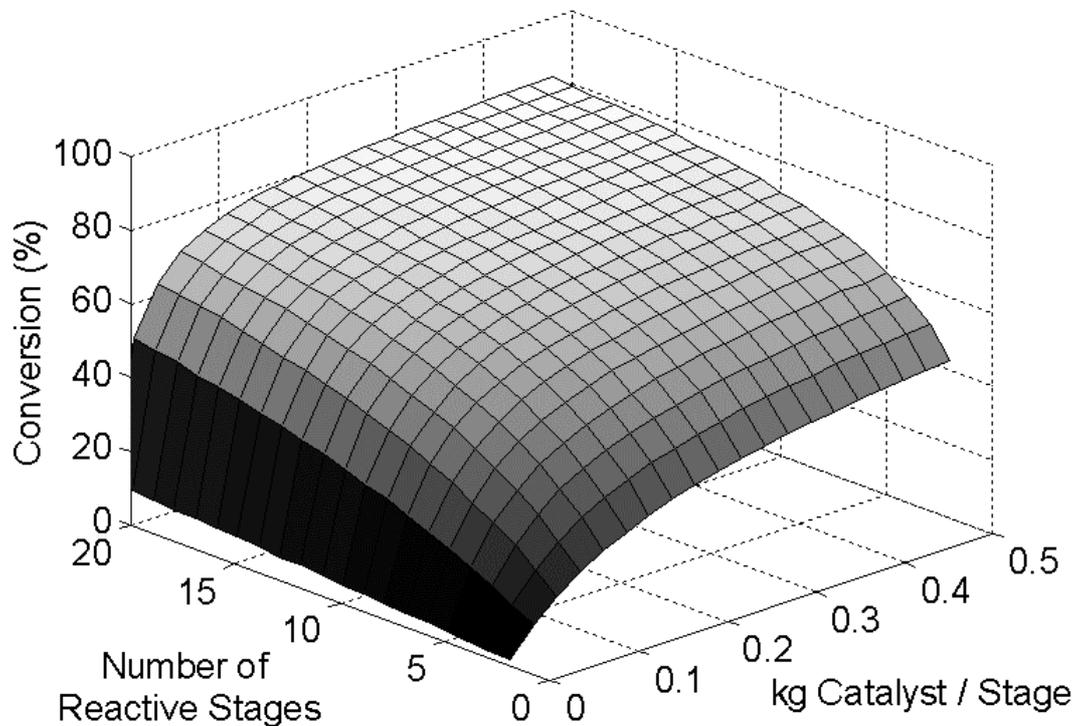


Figure 11. Influence of amount of catalyst per stage and number of reactive stages ($\dot{F}_{MeOAc} = \dot{F}_{BuOH} = 0.02 \text{ kmol h}^{-1}$; $D:F = 0.51$; $v = 1$; $P = 1 \text{ bar}$; 5 non-reactive stages above and below the reactive section)

A comparison of the performance of Katapak[®]-S and Katapak[®]-SP is given in Figure 12. It can be seen that for a column pressure of 1 bar, Katapak[®]-SP shows a better performance since higher conversions can be obtained with the same packing height. For higher pressures, the influence of the reaction kinetics and therefore the advantage of Katapak[®]-SP which offers higher amount of catalyst per section, decreases and both packings show nearly the same performance. But even a large reactive section does not lead to sufficient conversions.

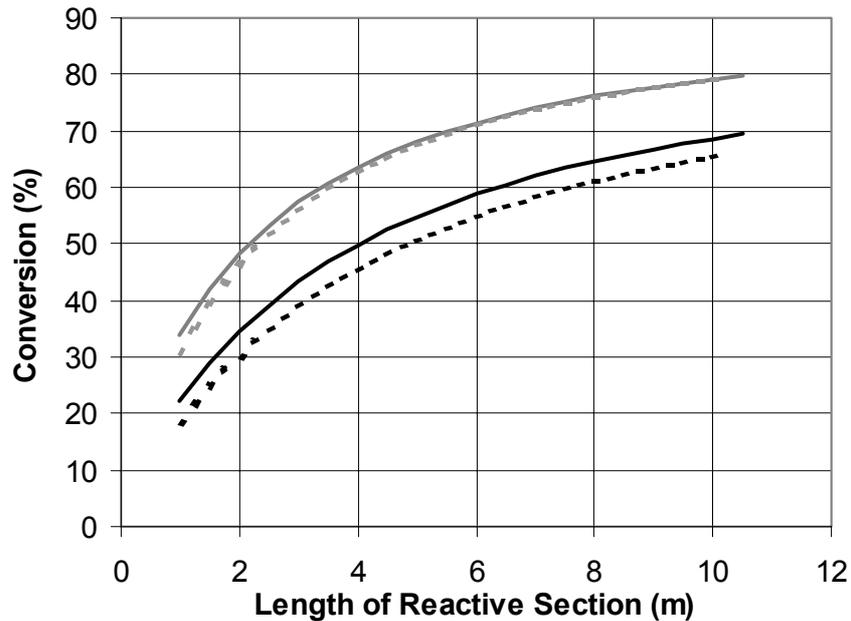


Figure 12. Influence of the packings ($\dot{F}_{MeOAc} = \dot{F}_{BuOH} = 0.02 \text{ kmol h}^{-1}$; $D:F = 0.51$; $v = 1$; 5 non-reactive stages above and below the reactive section; light gray: $P = 1.8 \text{ bar}$; black: $P = 1 \text{ bar}$; Katapak[®]-SP: —; Katapak[®]-S: — —)

A further option in reactive distillation processes to obtain high conversions is the application of a prereactor. Chemical equilibrium can be obtained in the prereactor and the reactive distillation column should enhance the conversion to nearly 100%. Figure 13 shows the application of a prereactor. n-Butanol and a given percentage of methyl acetate is fed into the prereactor. Additionally methyl acetate is directly fed into the column below the reactive section. Figure 13 shows the conversion of the overall process as a function of the quantity of methyl acetate fed into the prereactor. It can be seen that at about 55% of methyl acetate fed into the prereactor the maximum overall conversion is achieved. However it should be mentioned that overall conversions are not significantly above the conversions which can be achieved without a prereactor (conversion of about 50%, Figure 8).

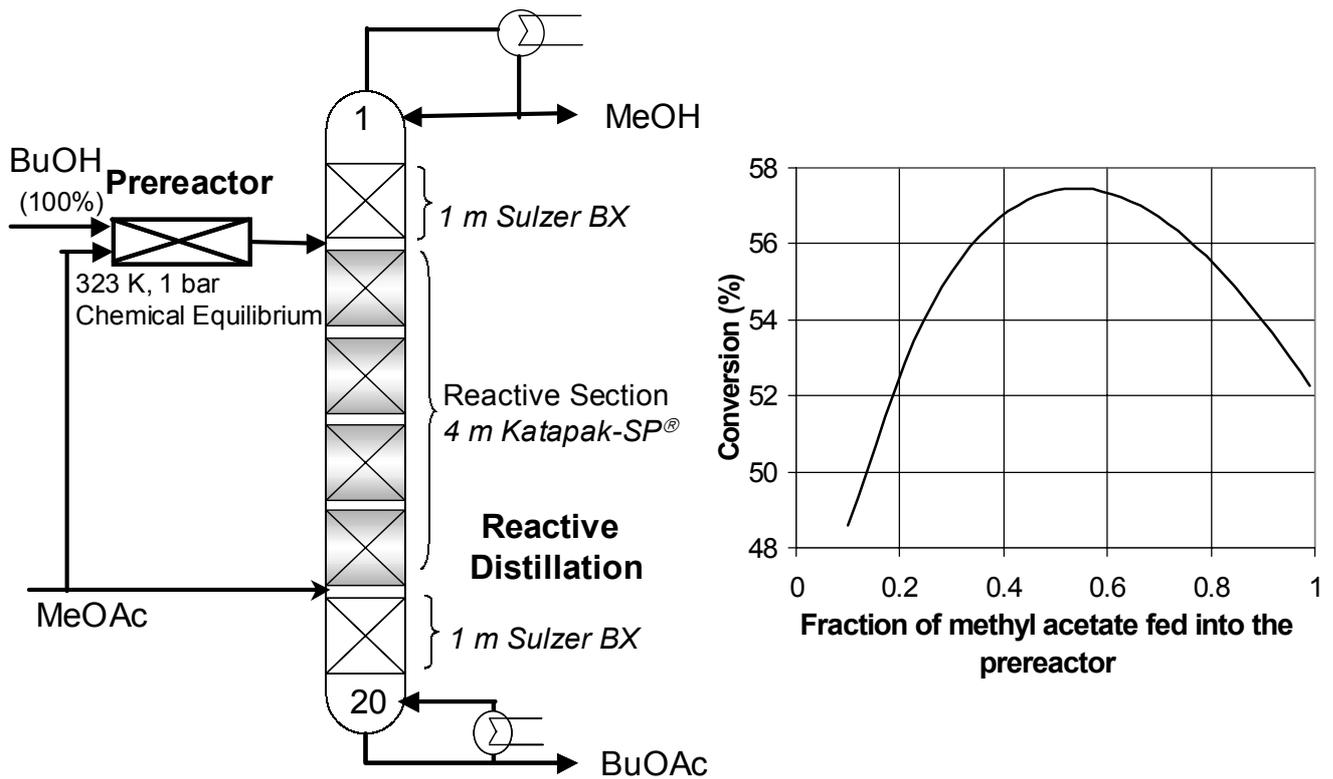


Figure 13. Application of a prereactor

$$(\dot{F}_{MeOAc} = \dot{F}_{BuOH} = 0.02 \text{ kmol h}^{-1}; D:F = 0.51; v = 1; P = 1 \text{ bar})$$

Elevating the pressure is not an option also for this process since temperatures inside the reactive section are above 393 K at pressures around 1.8 bar. It can be concluded from Figure 13 that the application of a prereactor does not result in higher overall conversions and therefore further separation processes have to be combined with reactive distillation. The combination of reactive distillation with pervaporation, results in a process where high conversions can easily be obtained as shown in Figure 14. This figure shows the performance of the process if an ideal pervaporation process is assumed. This means that unreacted methyl acetate is completely refluxed into the column and that the methanol is completely separated from the distillate stream by pervaporation. It is clear from the previous section that this process cannot be realized with a Pervap 2250-60 membrane. Other membranes like the cuprophane membranes will be tested soon and it will be shown that the assumption of this ideal pervaporation process can be realized with a multistage pervaporation process [18].

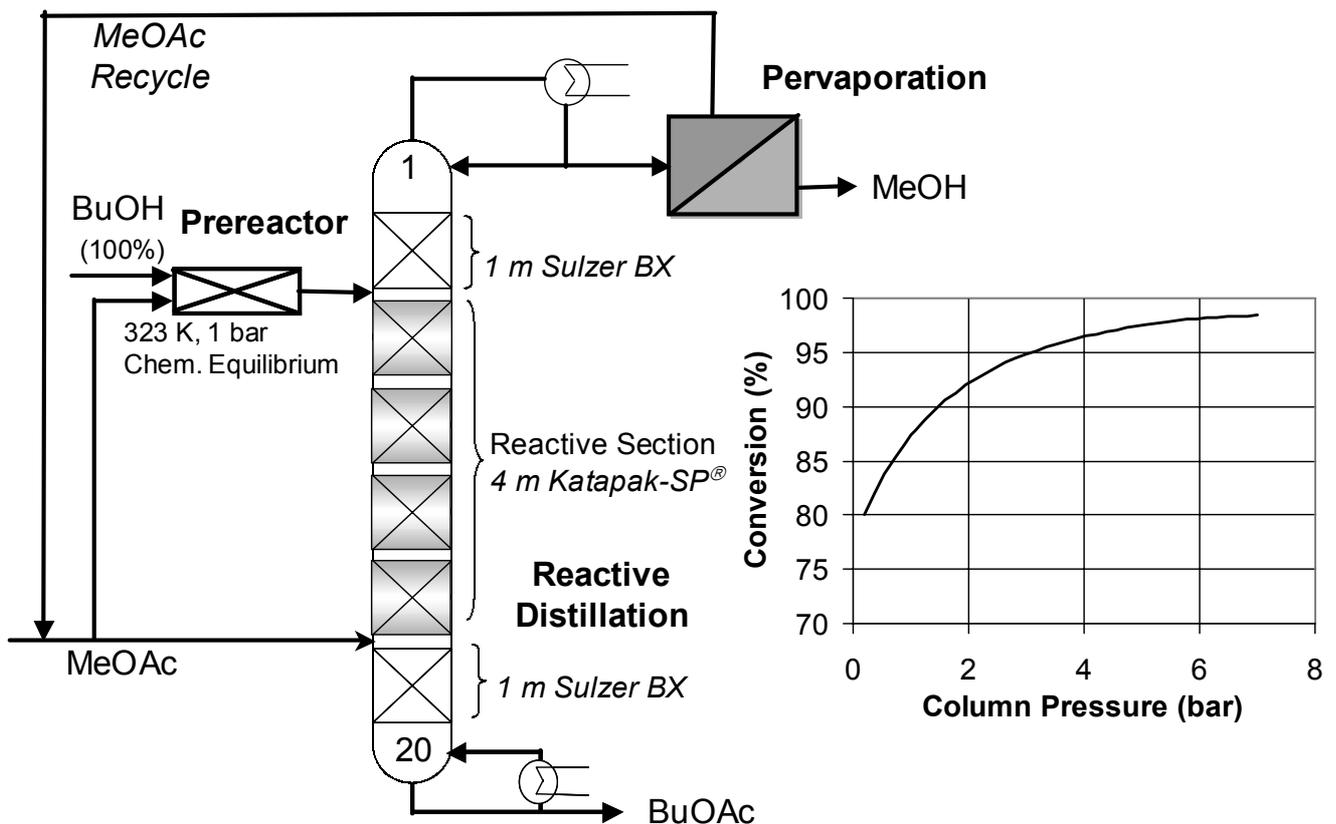


Figure 14. Combination of reactive distillation with ideal pervaporation
 ($\dot{F}_{MeOAc} = \dot{F}_{BuOH} = 0.02 \text{ kmol h}^{-1}$; $D:F = 0.75$; $v = 1$; 80% of methyl acetate is fed into the prereactor).

It can be seen that a conversion close to 100% can be achieved at elevated pressure. Temperatures at 393 K are reached (which is the maximum operating conditions for typical ion-exchange resins) in the reactive section above 4 bar and the proposed process is capable of producing n-butyl acetate and methanol with conversions of 97%. As can be seen from Figure 15 the separation efficiency of the membrane is crucial to the success of the proposed process. The conversion of the overall process of course will decrease with an increasing fraction of methyl acetate present in the permeate.

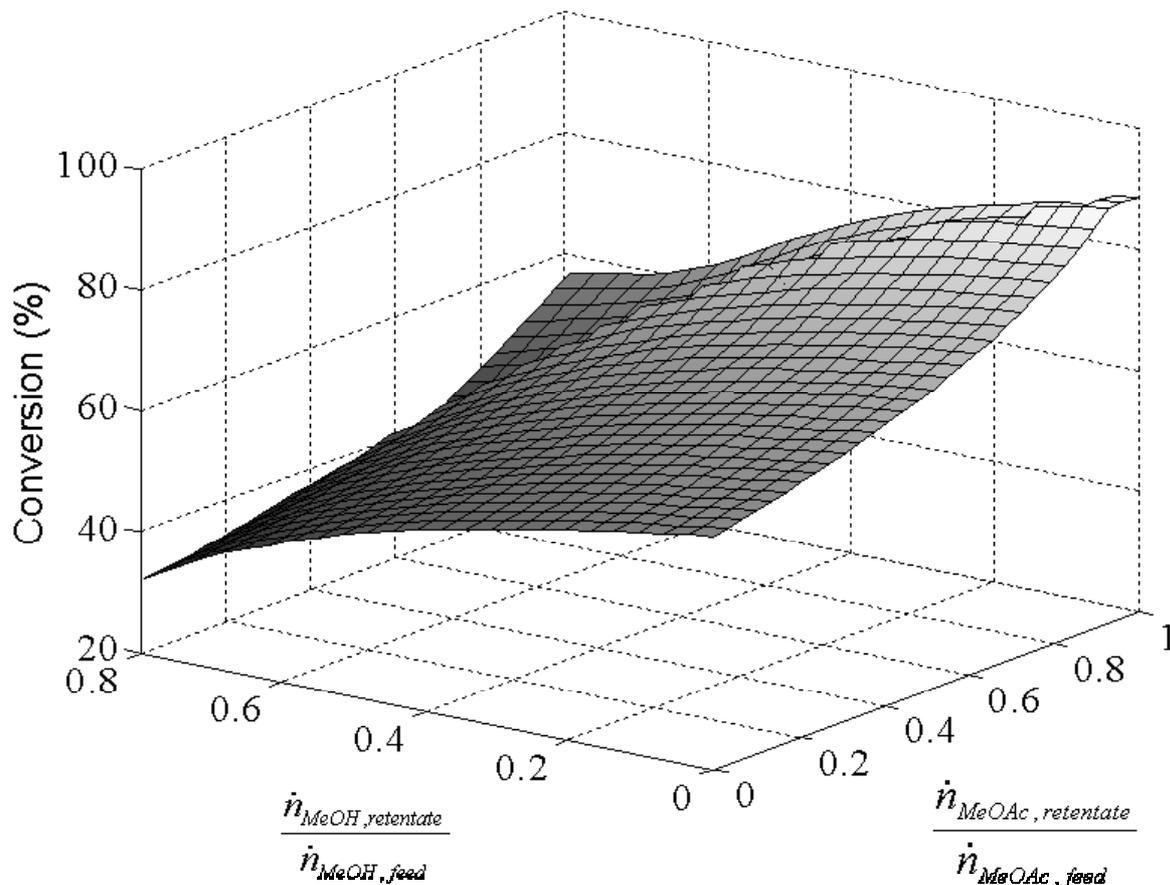


Figure 15. Influence of the separation efficiency of the membrane on the conversion ($\dot{F}_{MeOAc} = \dot{F}_{BuOH} = 0.02 \text{ kmol h}^{-1}$; $D:F = 0.75$; $v = 1$; $P = 1 \text{ bar}$; 80% of methyl acetate is fed into the prereactor).

High overall conversions are possible when selective membranes are applied. Therefore further membranes will be tested to optimize the process. All further calculations will therefore assume an ideal pervaporation process, i.e. methanol is completely obtained as permeate and methyl acetate is completely recycled into the column. Traces of n-butyl acetate and butanol which might be present in the distillate are also refluxed into the column with the recycle stream. Figure 16 shows the influence of the amount of catalyst per reactive tray for a 50 mm diameter column and the influence of the number of reactive stages for the process presented in Figure 14.

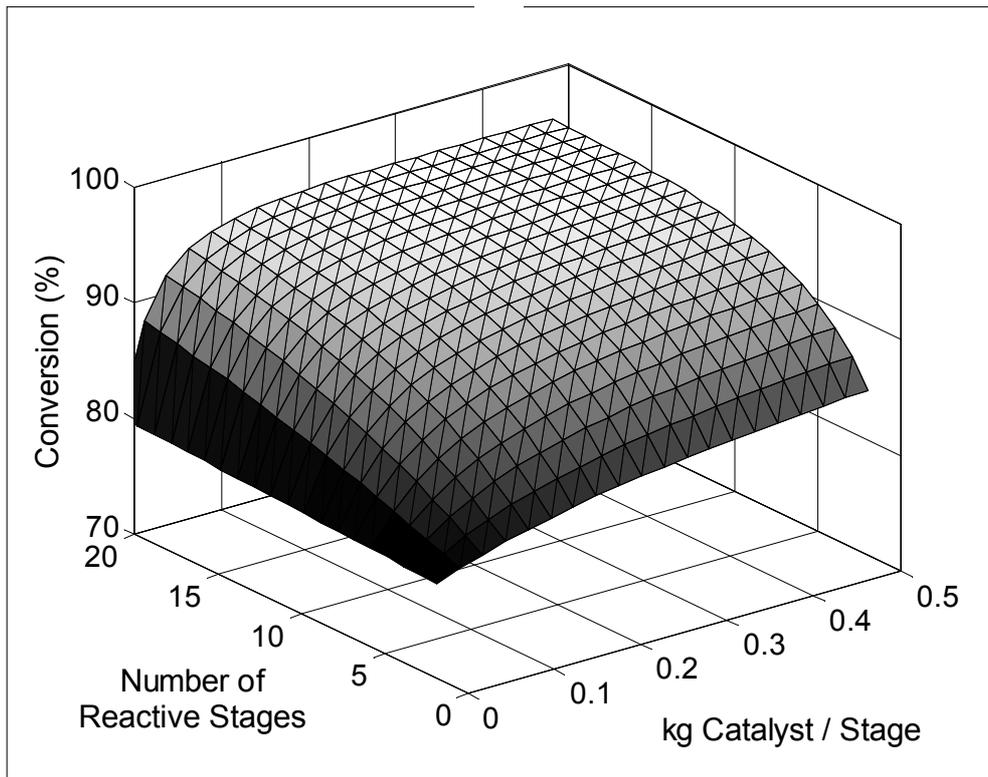


Figure 16. Influence of amount of catalyst per stage and number of reactive stages ($\dot{F}_{MeOAc} = \dot{F}_{BuOH} = 0.02 \text{ kmol h}^{-1}$; $D:F = 0.51$; $v = 1$; $P = 1 \text{ bar}$; 5 non-reactive stages above and below the reactive section, 80% of methyl acetate is fed into the prereactor)

It can be seen that overall conversion can significantly increased using the proposed process. Figure 17 shows the influence of Katapak[®]-S and Katapak[®]-SP on the performance. It can be concluded that both, separation efficiency and amount of catalyst per section are important and that Katapak[®]-SP shows better results for lower pressure. At higher pressures the separation efficiency becomes more important and Katapak[®]-S shows better characteristics. Furthermore it can be seen that conversions close to 100% can be achieved with a reasonable size of the reactive section.

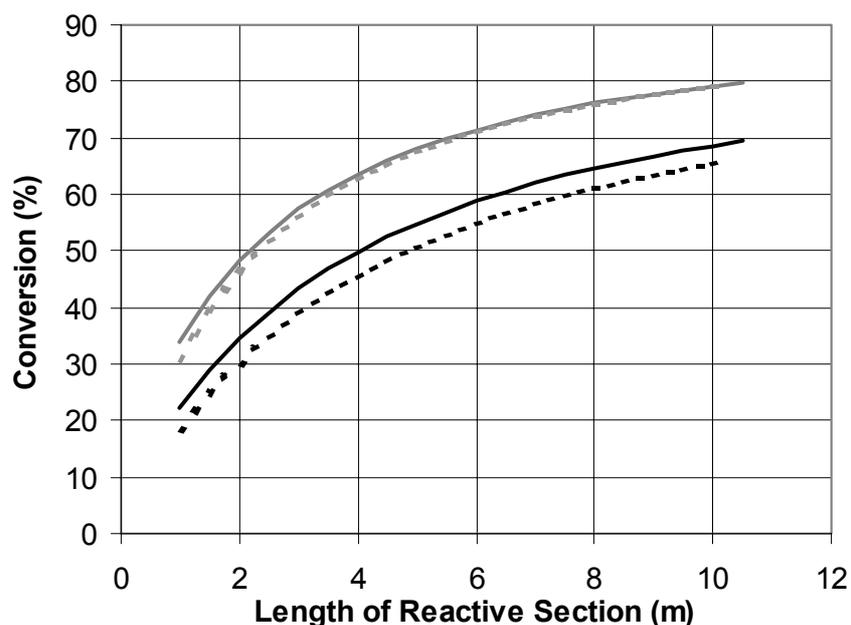


Figure 17. Influence of the packings ($\dot{F}_{MeOAc} = \dot{F}_{BuOH} = 0.02 \text{ kmol h}^{-1}$; $D:F = 0.51$; $v = 1$; 5 non-reactive stages above and below the reactive section; 80% of methyl acetate are fed into the prereactor; light gray: $P = 4 \text{ bar}$; black : $P = 1 \text{ bar}$; Katapak[®]-SP: —; Katapak[®]-S: — —)

The previous evaluation permits us to present an optimized process. Assuming that an ideal pervaporation process can be achieved and that the prereactor works at chemical equilibrium, about 7 m Katapak[®]-S or Katapak[®]-SP are necessary. Higher total feed rates would require a larger reactive section as can be seen from Figure 9. Five theoretical stages above and below the reactive section are necessary in order to ensure a sufficient stripping of methyl acetate in the lower part and a separation of n-butanol from methanol and methyl acetate in the upper part of the column. A reflux ratio of unity can be proposed and 80% of methyl acetate should be fed into the prereactor. High D:F-ratios should be realized. A pressure of 4 bar is recommended. The application of a thermally more stable catalyst would allow to increase pressure and to reduce the size of the reactive section.

CONCLUSION

A method for the development of kinetically controlled reactive distillation processes is presented. The thermodynamic aspects of the model reaction, the transesterification of methyl acetate with n-butanol forming n-butyl acetate and methanol, have been discussed and UNIQUAC interaction parameters have been determined using the Dortmund Data Bank (DDB). The reaction kinetics of the reaction has been investigated and kinetic constants for the pseudohomogeneous model are derived. The results are incorporated into the process simulator Aspen-Plus (RADFRAC). Pervaporation measurements for the separation of the binary mixture methyl acetate – methanol have been performed. Several measurements using a pilot-plant reactive distillation column equipped with Katapak[®]-S and Katapak[®]-SP packings have been performed and the

influence of important operating conditions (reflux ratio, total feed rate) has been studied experimentally and by simulation. It has been shown that simulation results are in a good agreement with experimental data. This reliable simulation can therefore be used for process modeling and optimization. The influence of several important design factors and operating condition on the performance has been determined. It has been shown that higher pressure require thermally more stable catalysts and that even a large number of reactive stages does not lead to sufficient conversions. Even the application of a prereactor does not lead to significant increase of the conversion. Therefore a new process, the combination of reactive distillation with pervaporation, is proposed and it has been demonstrated that conversions close to 100% can be achieved with a reasonable size of the reactive section. Crucial to the success of this process is the availability of an appropriate membrane which is capable of splitting the methyl acetate – methanol binary mixture which is present in the distillate stream of the reactive distillation column. Further membranes will be tested in order to ensure the applicability of the process.

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