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# Acetalization reaction of ethanol with butyraldehyde coupled with pervaporation. Semi-batch pervaporation studies and resistance of HybSi<sup>®</sup> membranes to catalyst impacts

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## ABSTRACT

Acetals are seen as important bio-based diesel additives. The production of these compounds from an alcohol and an aldehyde suffers from low conversions due to thermodynamic limitations. These limitations can be overcome through the continuous removal of the by-product water. One of the most promising innovative reaction systems is a membrane reactor equipped with a dehydration membrane. Water selective organic/inorganic HybSi<sup>®</sup> membranes were used for this purpose. As a representative example the production of 1,1 diethoxy butane from ethanol and butyraldehyde was studied. Permeance data were determined from pervaporation dehydration experiments using non-reacting quaternary mixtures at various temperatures. Membrane reactor experiments show that the conversion of the acetalization reaction can be increased from the thermodynamic value of 40% to 70% at 70 °C and a stoichiometric initial composition. The reactor experiments could be predicted using kinetic data of the reaction and a simple empiric membrane performance relation. The chemical stability of the membrane in the presence of aggressive organic solvents, like butyraldehyde, and its mechanical resistance against the solid catalyst particles of Amberlyst 47 were shown to be satisfactory.

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## 1. Introduction

One of the first pervaporation processes studied using a dehydration membrane was the removal of water from ethanol–water mixtures. One of the advantages of doing this separation by using a pervaporation membrane is that complex distillation that is required to break the azeotrope can be avoided. Through the integration of distillation and a membrane step, high separation yields at relatively low capital and operational costs can be achieved [1]. In the recent years several dehydration membranes as well as membrane processes for the production of ethers and esters were developed [2–6].

Acetals are prepared in an equilibrium reaction between an alcohol and an aldehyde with water as a by-product. The thermodynamic limitations in conventional reaction systems result in low conversions for these reactions [7–11]. Sanchez Marcano and

Tsotsis [12] were among the first to describe the advantages of a membrane reactor for the applications. The continuous removal of water from the reaction mixture through the application of a pervaporation membrane shifts the reaction to the product side and thus increases the yield [2,3,13–17].

Acetalization reactions are homogeneously catalyzed using strong mineral acids such as H<sub>2</sub>SO<sub>4</sub>, HF, HCl or p-toluene sulphonic acid [18–20]. The intrinsic disadvantage of these catalysts, corrosive and environmental properties, entails uneconomic processes and it has led to the development of solid acid catalysts. Capeletti et al. [7] reported the performance of several solid acid catalysts, from commercial, natural and laboratory sources. They concluded that ion exchange resins show better performance than other catalysts reaching equilibrium faster than using other alternatives.

In coupled pervaporation–reaction systems, the reaction and the separation can be carried out in one unit using catalytically active membranes [5,21,22] or in a conventional batch reactor with the membrane separation in a recycle loop [2,3,16,17,23]. The retentate, all the components except water, are then returned to the reactor. A third option would be to combine the reaction and separation in one single unit by using a non-catalytic membrane and an additional catalyst. This option offers more flexibility as the amount of catalyst and the membrane area become decoupled. Also different lifetimes can be accommodated easier as they can be replaced

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independently. In the present article, we propose this decoupled option for the first time for acetalization reactions.

Another important classification concerns the membrane material, with the two main classes being ceramic and polymeric. In esterification processes, where the pervaporation unit is not integrated in the reaction unit, most of the articles report the use of commercial polymeric dehydration membranes [2,3,16,23], whereas in those processes where the reaction and the separation are combined in one single reactor polymeric, ceramic and polymeric/ceramic membranes are applied [5,13,21,22,24].

In this work a hybrid silica membrane (HybSi<sup>®</sup>, developed at ECN) for dehydration was used. This HybSi<sup>®</sup> membrane has a very high hydrothermal stability and can be used in the dehydration of various organics [25–29]. This membrane was used in pervaporation testing of binary (ethanol–water) and in the dehydration of multi-component mixtures which contained all reactants and products. These permeation results were used as input into a batch reactor model. Subsequently, the membranes were used in a reactive system containing ethanol, butyraldehyde, 1,1 diethoxy butane, water and Amberlyst 47 as catalyst. The influence of the membrane under different process conditions (temperature, feed concentrations, catalyst loading) on the conversion was determined. A simple batch model was used to check the assumptions that will be used later in a continuous process design study and to assess the feasibility of the membranes in this novel process. The design of a continuous process and the supporting tests will be reported elsewhere.

## 2. Experimental procedure and equipment used

### 2.1. Chemicals and catalyst

Ethanol (99.9%, w/w) and butyraldehyde (99%, w/w) from Merck were used as reagents. 1,1 diethoxy butane (97%, w/w) for GC calibration was obtained from Acros Organics. Amberlyst 47 sulphonic ion exchange resin kindly provided by Rohm and Haas was used as catalyst.

### 2.2. Membrane

In the present study HybSi<sup>®</sup> inorganic/organic hybrid membranes were used. The hybrid nature of this material lies in the fact that each silicon atom is not only connected to oxygen atoms as in pure silica, but also to an organic fragment. The special feature of HybSi<sup>®</sup> is that the organic fragments are acting as integral bridging fragments rather than as end standing groups as in methylated silica [25,30].

HybSi<sup>®</sup> membranes are prepared via a sol–gel process and by coating the sol on top of a tubular porous support. The membranes show a high stability in the dehydration of *n*-butanol (5 wt% of water) at 150 °C, and were tested for more than 2 years [27,28]; moreover they show a great chemical resistance to acid containing liquid mixtures [26,29]. Apart from the durability and chemical resistance HybSi<sup>®</sup> membranes present high water selectivity and a high water flux as compared to other available membranes [31]. The separation factors for the separation of water from ethanol are around 220 and water fluxes are around 0.8–1.5 kg m<sup>-2</sup> h<sup>-1</sup> [29]. Because of this, HybSi membranes seem to be good candidates to remove the water from an acetal producing reaction mixture without being deteriorated by catalyst particle impacts and the presence of aggressive organic compounds like butyraldehyde.

### 2.3. Analysis

In case of the binary mixture dehydration tests, both, feed and permeate side mixtures were analyzed through refraction

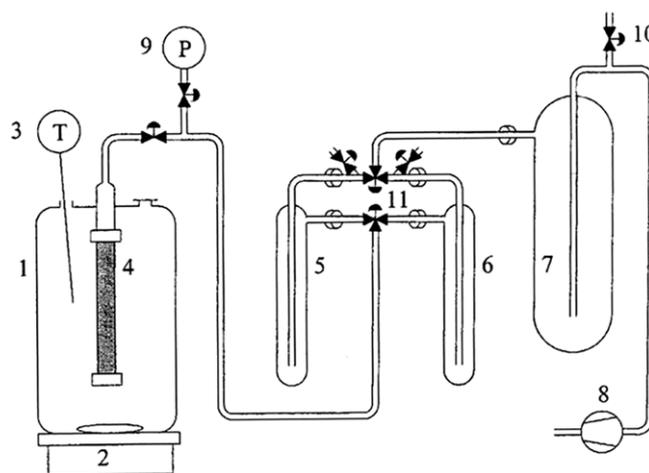


Fig. 1. Simplified schematic drawing of the glass pervaporation unit.

index measurements at 20 °C. The analyses of the quaternary mixture were more complicated. The water content of the feed was measured using Karl Fischer titration method. The contents of the organic components ethanol, butyraldehyde, and 1,1 diethoxy butane were determined by gas chromatography (Shimadzu GC-17A) using a flame ionization detector (FID). A Phenomenex ZB-Wax plus capillary column was used (30 m × 0.25 mm × 0.25 μm) with helium as the carrier gas. In the permeate, the water content was estimated using refraction index. Initial analyses has shown that water and ethanol were by far the main species in the permeate and that small amounts of butyraldehyde and 1,1 diethoxy butane did not affect to the refraction index measurements. The water concentration in the permeate calculated as the difference from 100% of the organics sum was in good agreement with the concentration obtained from refraction index measurements.

### 2.4. Reaction–pervaporation system

The experiments were carried out in a semi-batch lab scale glass pervaporation unit. The glass pervaporation equipment is made up of three parts:

- Feed system consisting of a feed vessel of 1.6 L (1), heating/stirring plate (2), stand and membrane (the membrane area used in the experiments was 24.2 cm<sup>2</sup>) immersed in the feed mixture (4). There is also an option to use a feed pump to add liquid to the feed.
- Continuous permeate extraction system which consists of large chilled water spiral glass condenser and permeate vessel, chilled water unit, pressure sensor and vacuum pump.
- Permeate sampling system consisting of a connection to a permeate valve and sample vials (11), pressure sensor (9), liquid nitrogen cold trap and vacuum pump.

Samples are collected by condensing the permeate with liquid nitrogen in one of the sample vials. The purpose of the cold trap (7) is to ensure no vapors reach the vacuum pump and/or the atmosphere. The vacuum pressure sensors are connected to a central display unit and the permeate pressure was between 1 and 5 mbar in all the cases. A simplified schematic drawing is shown in Fig. 1.

## 3. Results and discussion

The reaction under consideration is the acetalization of ethanol (A) and butyraldehyde (B) to produce 1,1 diethoxy butane (C) and

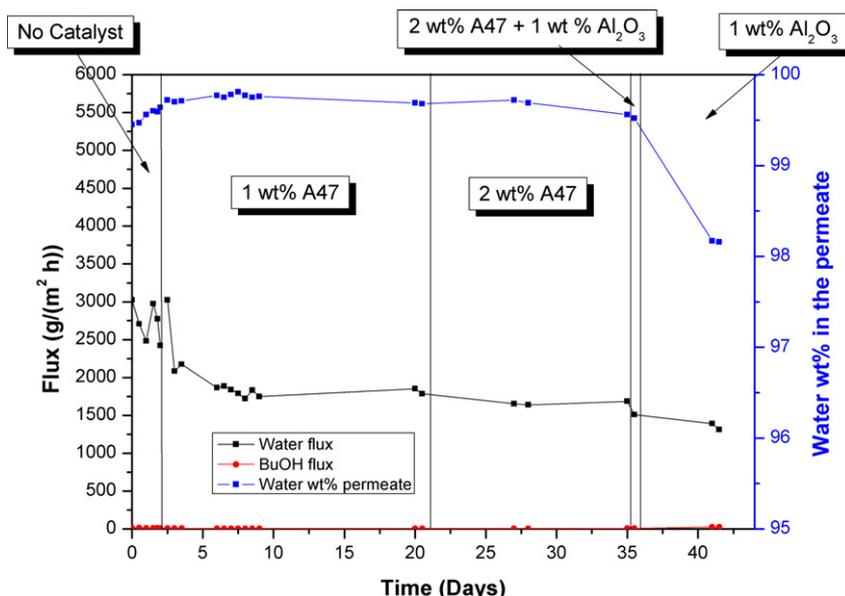
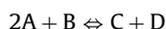


Fig. 2. Performance of the membrane in butanol/water mixture at 95 °C with different catalyst and alumina pellets loadings.

water (D):



As most of the acetalization reactions, this reaction is also exothermic and it shows high thermodynamic limitations [32] achieving low equilibrium conversions and it is catalyzed by acidic ion exchange resins. A pseudo-homogeneous kinetic model can describe the behavior of the reaction pretty well [32].

The experiments were divided in three different sets. First of all, the membrane mechanical resistance to the catalyst particle impacts was tested. Secondly, ethanol-butylaldehyde-1,1 diethoxy butane–water mixture dehydration experiments were carried out (without reaction) in order to check the membrane selectivity for this mixture and to obtain permeance values for each compound. Finally, experiments where both reaction and pervaporation happen were studied in the same unit. In parallel a semi-batch model was developed and used in order to predict the coupled pervaporation and acetalization reaction and to compare this with the experiments.

The transport equation for a certain component through the membrane was the based one on Fick's Law:

$$J_i = Q_i(x_i\gamma_iP_i^{\text{sat}} - y_iP^{\text{perm}}) \quad (1)$$

The saturation pressure of each pure component was calculated with the corresponding Antoine's equations [33]. Activity coefficients were calculated with the NRTL model for ethanol/butylaldehyde/1,1 diethoxy butane/water mixtures [34]. In case of binary mixtures after several preliminary calculations using different models the Margules [35] one was selected because of it is the easiest one to be used and gave comparable results.

### 3.1. Mechanical resistance to catalyst particle impacts

One important test was to check if the presence of Amberlyst 47 resin particles could damage the membrane surface and deteriorate the membrane performance. Depending on the membrane behavior, the experimental setup (a slurry reactor) could be modified to avoid this effect. Sommer and Melin [36] observed a selectivity drop after some small metal particles crashed over a silica membrane. Abrasion of the membrane top-layer was determined and

they recommend installing a filter in order to prevent the collision of particles on the membrane surface.

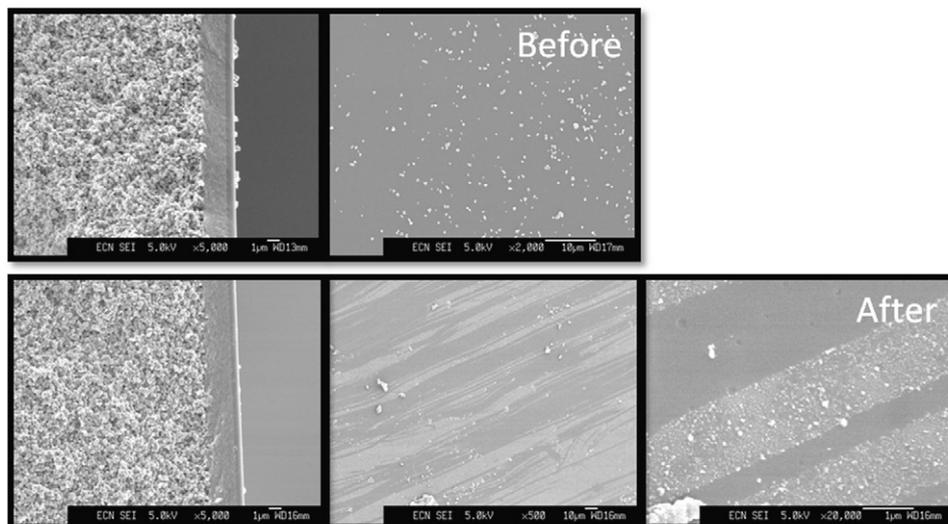
The (pervaporation) test was carried out with a butanol/water (95/5 wt%) binary mixture at 95 °C and 1200 rpm and the membrane was continuously tested in this mixture. The experiment was divided in 4 different time intervals. During the first few days no catalyst was added and the membrane behavior was checked and followed as function of time. In this region the flux decreased somewhat and the water concentration in the permeate increased a bit. This behavior is commonly observed for HybSi membranes during the first 10 days of operation. The permeate contained about 99.5% water showing a high selectivity for this separation. Afterwards 1 wt% of catalyst was added to the mixture and during 18 days no change in the membrane behavior was observed (see Fig. 2). It was observed that catalyst particles broke up due to the magnetic stirring system. The particle size decreased from 0.9 mm to some microns, as measured by microscopy. At this stage, an additional 1 wt% of fresh catalyst was added. Again, the membrane performance did not change and catalyst particles broke up. A more aggressive test was done with 1 wt% of harder alumina extrudates (length: 3.1 mm, diameter: 2.85 mm) added to the mixture. In this case the water purity in the permeate decreased from 99.5% to 98% after 8 days of impact testing (see Fig. 2). Once more, all the alumina pellets broke up into particles of a few microns.

To assess the damage done to the membrane SEM micrographs (Fig. 3) of the cross section and surface we taken after the experiment, and compared to those of a piece from the same membrane tube. This latter piece shows the membrane "as prepared". The cross section SEM picture are comparable with well defined layers. The SEM pictures taken from the membrane surface show an increased amount of deposits or sediments attached to the surface. It is likely that this particles find their origin in the catalyst or alumina pellets. Also some mechanical effects or scratches seem to have appeared.

It can be concluded that the membrane showed a great resistance to the impacts of the Amberlyst catalyst for a period of more than 30 days. Only when harder particles (alumina pellets) were added a slight selectivity decrease was observed.

### 3.2. Quaternary dehydration experiments

Binary ethanol/water and quaternary ethanol/butylaldehyde/1,1 diethoxy butane/water dehydration pervaporation experi-

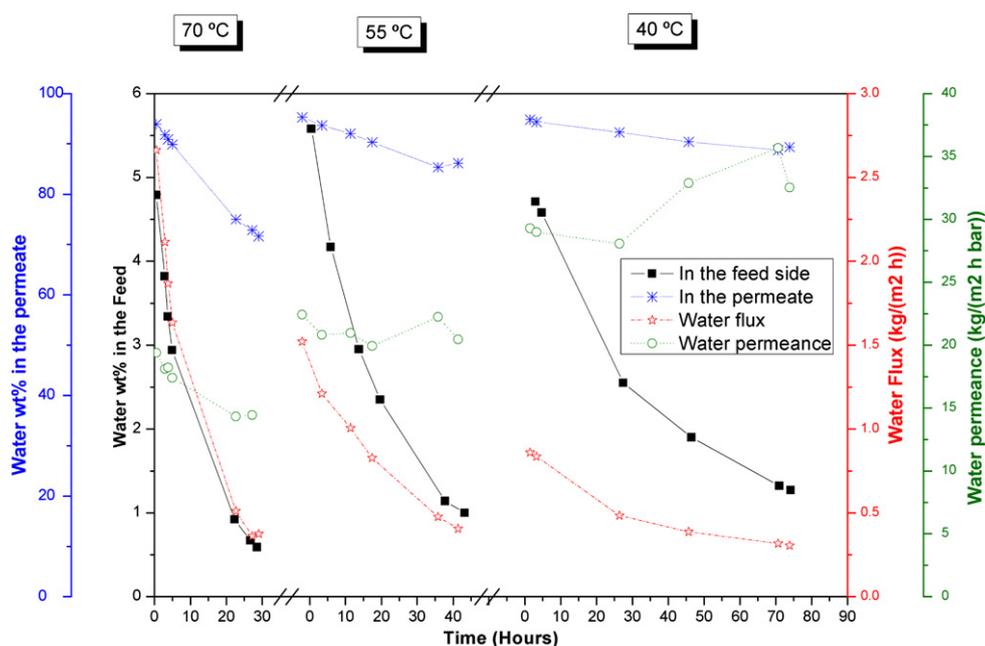


**Fig. 3.** SEM pictures of the membrane surface and membrane layers. Pictures were taken before (top) and after (bottom) the butanol/water experiments with Amberlyst resin catalyst and alumina pellets (the two left hand side pictures are from the cross section of the membrane, the top right and two bottom right pictures are from the membrane surface).

ments were carried out. The binary butyraldehyde/water and 1,1 diethoxy butane/water systems were not studied as these binary mixtures are not miscible in a relevant composition ranges. The aim of these experiments was to check the membrane behavior and confirm the suitability of this membrane for this specific mixture. The quaternary mixture was prepared by a simple reaction between ethanol and butyraldehyde in a batch reactor at 60 °C and with 1 wt% of Amberlyst 47 catalyst until equilibrium (30.8 wt% of ethanol, 24.1 wt% butyraldehyde, 40.1 wt% of 1,1 diethoxy butane and 5.0 wt% water was obtained in approximately 1 h) was reached. Subsequently, the catalyst particles were removed by filtering the mixture. Dehydration experiments using the mixture were carried out at 70, 55 and 40 °C, well below the bubble point of the mentioned mixture (77.8 °C calculated with Aspen Plus). These experiments were carried out in batch mode, so the water con-

centration in the feed continuously decreased during the experiment. The permeances used as input data for the semi-batch model were calculated from these experiments.

As Fig. 4 shows, the membrane is selective for the mentioned quaternary mixture achieving high water concentrations in the permeate. The water flux decreases about 40% when the temperature is decreased 15 °C; the water flux also decreases with a decreasing water concentration in the feed. These observations can be ascribed to a decreasing driving force for water transport. Further, the concentration of water in the permeate decreases with decreasing water content in the feed, consistent with a constant selectivity. It can be observed that at 70 °C it takes 20 h to go from 5 wt% of water to 1 wt% while at 40 °C it takes more than 80 h. However, the water concentration in the permeate does not change significantly with the temperature at the same feed water concentrations.



**Fig. 4.** Water concentration profiles and water flux versus time for 3 different experiments carried out at 70, 55 and 40 °C.

**Table 1**

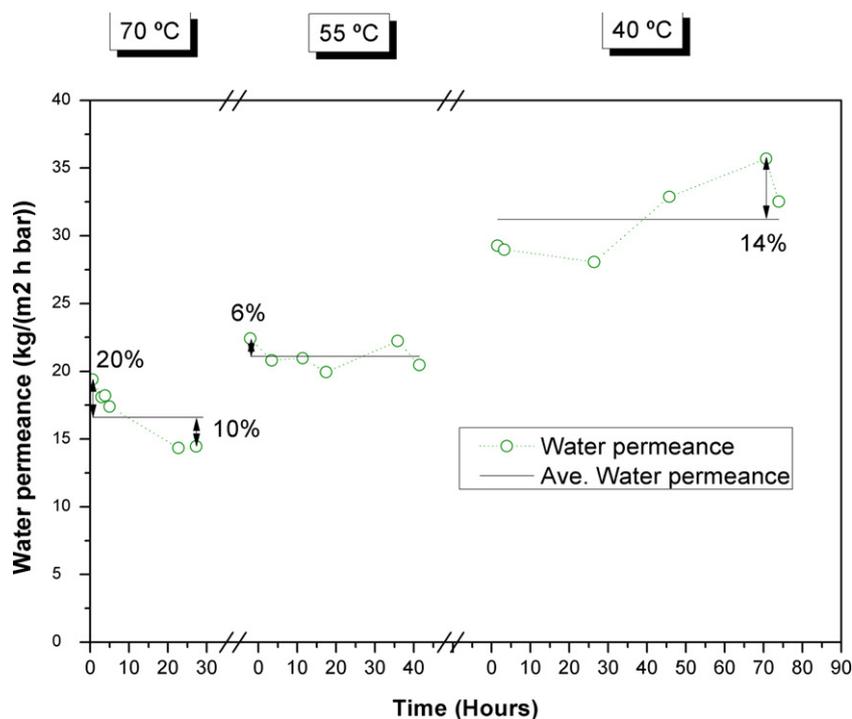
Average permeance values at 70, 55 and 40 °C for all the components and the corresponding fitting parameters.

	Permeance [mol/(m <sup>2</sup> h bar)]			Q <sub>0</sub> [mol/(m <sup>2</sup> h bar)]	E <sub>a</sub> [kJ/mol]
	70 °C	55 °C	40 °C		
Q EtOH	8.3 ± 1.4	8.5 ± 0.9	8.1 ± 1.5	10.92 ± 1.35	0.75 ± 0.7
Q but.	0.2 ± 0.07	0.1 ± 0.1	0.1 ± 0.0	(0.607 ± 0.015) × 10 <sup>3</sup>	23.0 ± 7.5
Q acetal	<0.17	<0.19	<0.18	0	n.a.
Q water	(0.92 ± 0.11) × 10 <sup>3</sup>	(1.17 ± 0.05) × 10 <sup>3</sup>	(1.73 ± 0.16) × 10 <sup>3</sup>	1.2 ± 2.1	-19.0 ± 2.1

The water permeance increases with decreasing temperature. A combination of different factors is believed to play a role here that influences the transport of species through the membrane: (1) sorption on the membrane, (2) diffusion through the membrane and (3) desorption from the membrane. Each of these effects has its own dependence on the temperature. With increasing temperature, sorption will become smaller while the diffusion rate increases. A decreasing permeance as function of temperature is observed when the heat of adsorption is larger than the respective activation energy for diffusion [37]. This effect is more commonly observed in gas transport, where the permeance of a strongly adsorbing gas, e.g. CO<sub>2</sub>, decreases with temperature, while for a none adsorbing component its permeance increases [38]. The influence of the feed water concentration on the permeance is less clear. At 70 °C the water permeance increases with increasing water content in the feed while at 55 °C there is hardly any dependence and at 40 °C the water permeance decreases with an increase of water content in the feed. The most likely explanation for this behavior is the difference in competitive adsorption between water and the organic components at different temperatures and concentrations. At a higher temperature there is less adsorption for both water and the organic component and water transport is less hindered by competitive adsorption. At lower temperatures the competition between the adsorption of water and the organic is stronger and even though the water flux increases with concentration (as the driving force increases) the permeance decreases. As it will be explained in Section 3.4, membrane changes as function of time are minimal and do not explain these permeance differences.

For the modeling study average values for the permeances were taken at each temperature (see Table 1) by fitting them to an Arrhenius' type correlation. As indicated in Fig. 4 the permeance is a function of the feed concentration and by taking an average permeance an error of maximum 20% is introduced (see Fig. 5). As shown further in Fig. 14, there is a good agreement between experimental and predicted data. This indicates that the assumption is acceptable within the process conditions used. When using the model outside the concentration range tested here, the influence of feed concentration on the permeance will have to be taken into account. The standard errors shown for butanal calculations are higher due to the measured small permeance values for this reactant as compared to the water permeance ones. Moreover, Fig. 6 shows that the linear trend lines fit fairly well to the data. For the acetal permeances, the indicated maxima were calculated from the detection limit of the analytic equipment for this compound. The acetal concentration in all the permeate samples was below this detection limit. By doing so, a simple empirical relation describing the performance of the used hybrid silica membranes within a rather small temperature and concentration range for the process under consideration is obtained. In Section 3.5, it is shown that this straight forward approach leads to a model that very well describes the discontinuous process.

The apparent activation energy (E<sub>a</sub>) is the sum of the activation energy of diffusion (E<sub>D</sub>) and the enthalpy of sorption (ΔH). While E<sub>D</sub> is generally positive, ΔH is usually negative for the exothermic sorption process. When the negative ΔH dominates over the positive E<sub>D</sub>, a negative value of E<sub>a</sub> occurs. A negative E<sub>a</sub>, and thus



**Fig. 5.** Assumed maximum errors taking average permeance values.

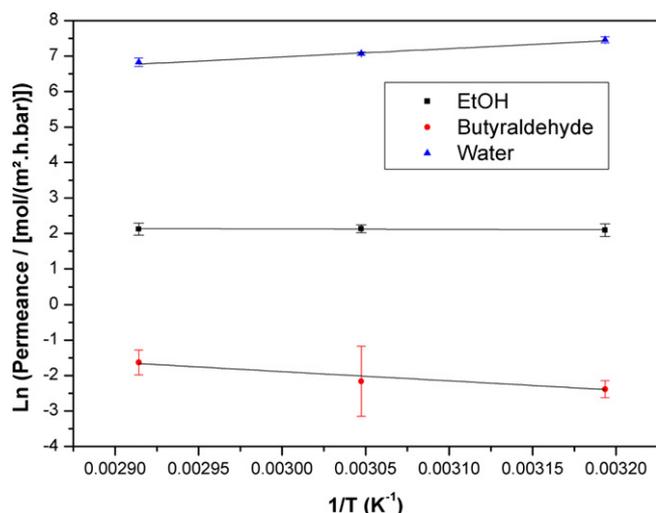


Fig. 6. Permeance data fitted to an Arrhenius type correlation.

a decreasing permeance with increasing temperature, does not mean that the flux will decrease when the temperature is increased. Often (as in the studied case) the flux increases with temperature because the effect of temperature on the saturation pressure, and thus driven force, is more significant [39]. The activation energy of  $-18.8$  kJ/mol for water using HybSi<sup>®</sup> membranes is close to  $-16$  kJ/mol as reported by Feng and Huang [39] using a polymeric membrane for ethanol–water dehydration experiments. Different activation energies for silica membranes for dehydration have been reported. ten Elshof et al. [40] has reported a value of  $-4 \pm 5$  kJ/mol for water in methanol and  $-24 \pm 7$  kJ/mol for methanol in a system containing 15 wt% water. Bettens [41] has reported water activation energies of between 8.5 and 13.5 kJ/mol for 90% water in respectively methanol and ethanol. Sommer and Melin [42] has reported an activation energy of 13.3 kJ/mol for water and 12.6 kJ/mol for ethanol for mixtures of 5–15 wt% water in ethanol. Differences in the activation energies could have to do with the type of membranes, competitive temperature dependent adsorption effects, different mixtures and test conditions.

### 3.3. Reaction + pervaporation experiments

Once the selectivity and the structural integrity of the selected membrane was proven, experiments with simultaneous reaction + pervaporation were carried out. The aim of these experiments was to demonstrate that the thermodynamic limitations of the studied reactions can be overcome. The influence temperature, catalyst loading, and initial composition were studied in a systematic manner. During the experiments, no side reactions were observed.

#### 3.3.1. Temperature effect

In Section 3.2, we saw that at higher temperatures increases the water flux through the membrane. However, as the acetalization is exothermic the equilibrium conversion decreases with increasing temperature, albeit with a higher reaction rate. The aim of these experiments was to determine the dominant process and the optimal temperature. For these purpose, three different temperatures were tested: 40, 55 and 70 °C, similar as used in Section 3.2.

Fig. 7 shows the typical process behavior. During the first 2 h all the concentrations changed considerably, more or less achieving the equilibrium concentration values corresponding to the initial composition and the used temperature. During this period the reaction kinetics and thermodynamics are predominant. After 2 h the water concentration reached a maximum and started decreasing due to the pervaporation process. In the mean time the acetal concentration started to increase above its equilibrium concentration. It is clear that the reaction rate is much faster than the pervaporation rate given the chosen experimental conditions. The membrane area is clearly too small ( $2.42 \times 10^{-3}$  m<sup>2</sup>) to remove the water fast enough from the reaction vessel of 1.6 L.

Fig. 8 shows the evolution of the conversion at the three selected temperatures using the same feed composition, catalyst loading and membrane. An increase of the temperature implies a decrease in the equilibrium conversion, as indicated by the dotted lines obtained from the kinetic studies carried out in a conventional batch reactor [32]. As discussed above, the water removal rate is higher at higher temperatures. This is reflected in the slope of the lines in Fig. 8. After roughly 15 h the order of the conversion rates inverts and the influence of the presence of the membrane becomes

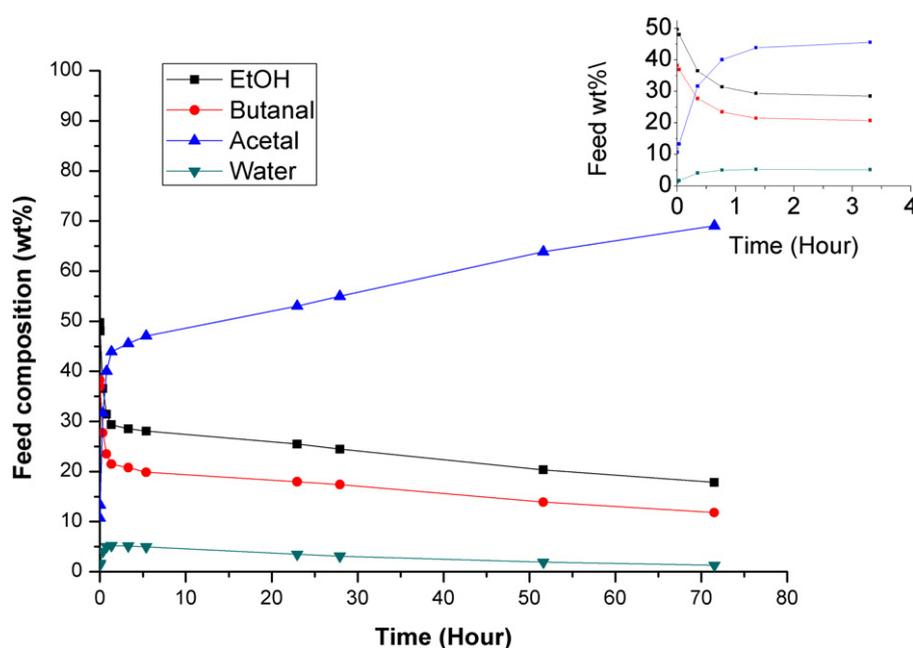


Fig. 7. Feed composition as function of time. Conditions: EtOH/butyraldehyde ratio: 2:1 in molar basis, 40 °C, catalyst loading 0.5 wt%.

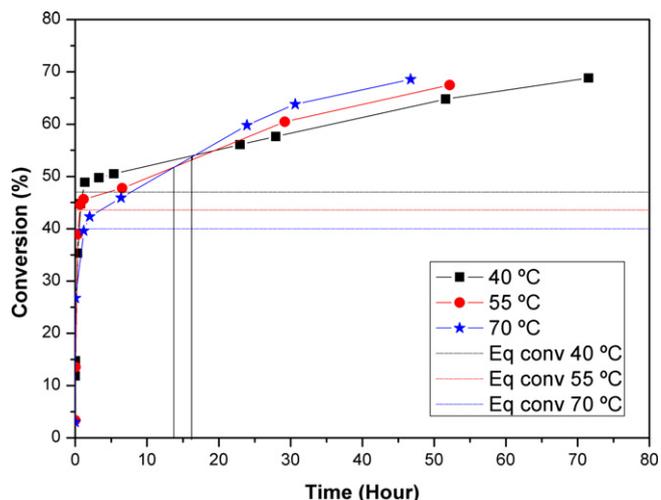


Fig. 8. Effect of the temperature and time on conversion. Conditions: ratio EtOH/Butyraldehyde 2:1 in moles, catalyst loading 0.5 wt%.

predominant. If a larger membrane area had been used, this period would have been shorter.

Fig. 9 shows the water concentration profiles on the feed side and on the permeate side. Following the previous reasoning, it can be observed that water concentration in the feed side showed a maximum in the 2nd hour and is higher at lower temperatures. This means that in the first 2 h, the reaction rate was much more important than the water removal by pervaporation since the membrane was not able to directly remove all the generated water. From the 2nd hour on, the overall reaction rate decreased and became adjusted to the requirements provided by the pervaporation as water extraction de-equilibrates the mixture and the pervaporation became the main conversion governing process. This leads to a decreasing water content in the feed and thus, an increase in conversion. The water concentration in the permeate increases during the first 2 h and then gradually decreases. This trend follows the water concentration in the feed. At lower temperatures the water concentration in the permeate is higher since the water concentration in the feed is also higher. The permeate composition during the first hours was mainly water and some ethanol. At the end of the experiment e.g. at 55 °C, the permeate concentration was the following one: 78.7 wt% water, 20.0 wt% ethanol, 1.3 wt% butyraldehyde and 0.4 wt% 1,1 diethoxy butane. This indicates that

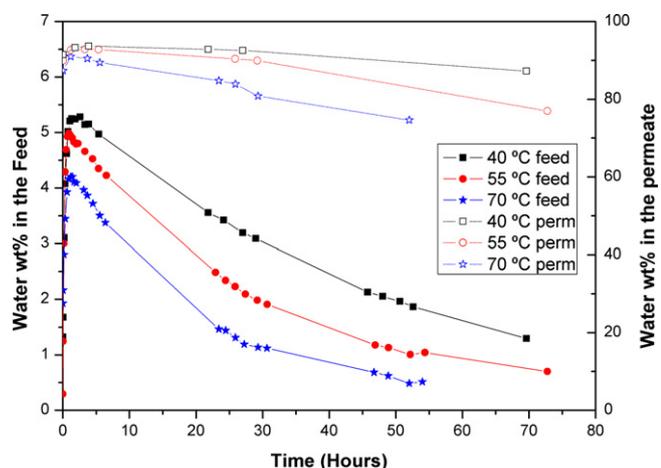


Fig. 9. Effect of the temperature and time on water profiles in the feed and in the permeate. Conditions: ratio EtOH/Butyraldehyde 2:1 in moles, catalyst loading 0.5 wt%.

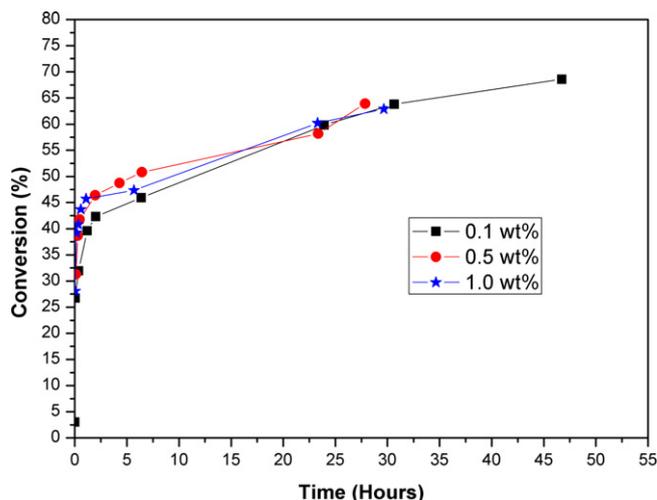


Fig. 10. Effect of catalyst loading on the process. Conditions: ratio EtOH:Butyraldehyde 2:1 in moles; temperature: 70 °C.

at low feed water concentrations of less than 1%, the permeate still contains a rather high water concentration.

### 3.3.2. Catalyst loading effect

The effect of catalyst loading was studied from 0.1 wt% to 1.0 wt%. at 70 °C, the temperature where the limiting effects of the membrane are smallest, (see Section 3.3.1) Fig. 10 shows that the catalyst loading has only a limited effect on the conversion and that pervaporation was still the limiting process. Small differences can still be observed. For example, at the lowest catalyst loading the equilibrium conversion (after about 2 h of reaction and pervaporation) was lower than at the catalyst loadings of 0.5 and 1 wt%.

### 3.3.3. Feed composition effect

To increase the conversion an excess of the cheapest reactant, ethanol, was used. The concentration of ethanol is also more affected by the pervaporation process than that of butyraldehyde. Apart from the stoichiometric molar feed ratio (2:1) also ratios of 2.5:1 and 3:1 were used. All the experiments were carried out at 70 °C and the used catalyst loading was 0.1 wt%. Fig. 11 shows the conversion profiles for the mentioned feed ratios. As expected, the higher the feed ratio the higher the conversion, In Fig. 12

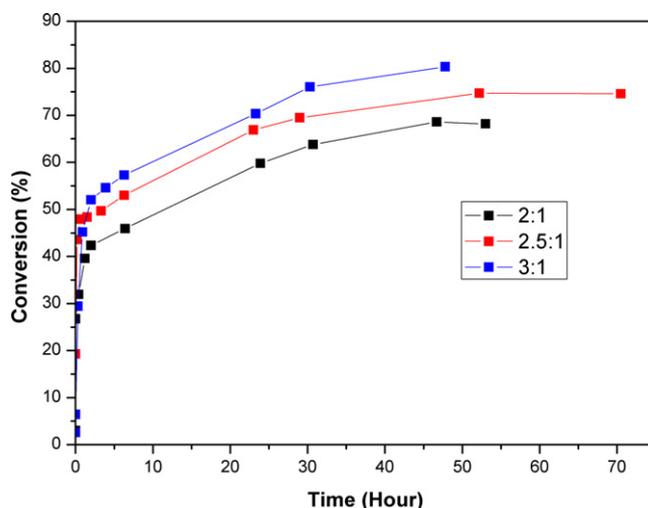
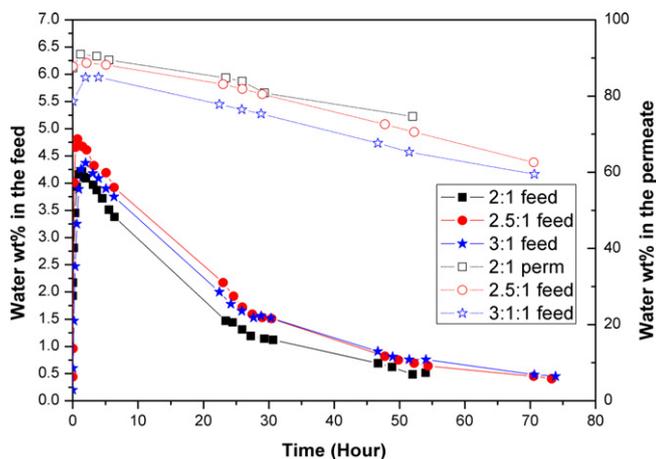


Fig. 11. Effect of the ethanol/butyraldehyde feed mole ratio on the process conversion. Conditions: temperature 70 °C, catalyst loading: 0.1 wt%.



**Fig. 12.** Effect of the ethanol/butyraldehyde feed mole ratio. Water concentration profiles both in the feed and in the permeate. Conditions: temperature 70 °C, catalyst loading: 0.1 wt%.

it can be observed that by increasing the ethanol/butyraldehyde ratio, the water concentration in the permeate side decreased. As the feed volume was constant in all the experiments, an increase of ethanol/butyraldehyde molar ratio implies a higher ethanol concentration and a lower butyraldehyde concentration. Thus, butyraldehyde is the limiting reactant and in spite of achieving higher conversions, the formed water is diluted by the excess of ethanol present in the feed side. In this way the water concentration in the feed side is lower at higher ethanol to butyraldehyde ratios and therefore its driving force is also lower. The excess of ethanol in the feed side implies a higher driving force through the membrane and therefore more ethanol passes through the membrane. As a consequence, the water concentration in the permeate side is lower than in the case of working with an initial stoichiometric feed concentration.

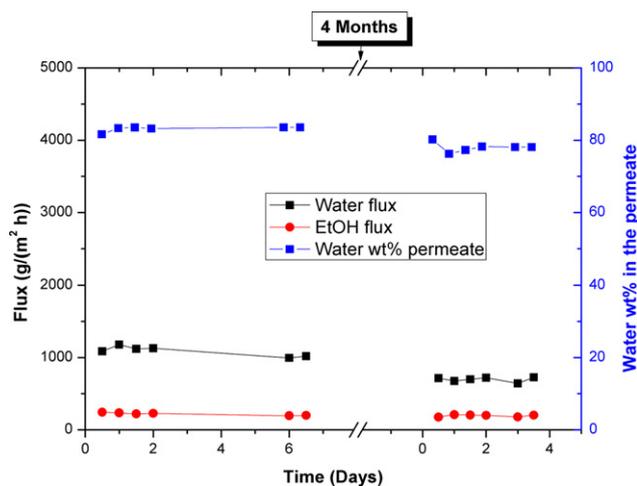
#### 3.4. Long term membrane performance

One single membrane was used for all the experiments presented in the Sections 3.2 and 3.3. The constant performance of this membrane is essential to assess the quality of these experiments. To this end we have tested the membrane in standard conditions (95:5 wt% ethanol:water at 70 °C) both at very start and at the very end of the 4 month measurement program. The results of these tests are depicted in Fig. 13. Over the whole measurement period both the flux and the permeate purity have slightly decreased. These minor changes in performance are commonly observed [29] even in a long term binary pervaporation test. In our assessment the membrane performance can be considered as constant during the duration of the current program of experiments.

#### 3.5. Modeling of batch “reaction + pervaporation” experiments and its validation

In an attempt to describe the behavior of the reacting mixture in the presence of a pervaporation membrane a model was made. In this simplified model we made the following assumptions:

- A pseudo-homogeneous kinetic model was assumed. The kinetic data of the reaction were obtained in the kinetic study performed in a conventional batch reactor [32].
- Perfect mixing was considered, i.e., there are no concentration and temperature gradients in the reactor.
- An isothermal process was assumed.



**Fig. 13.** Water flux and water concentration (wt%) in the permeate. Ethanol–water dehydration tests (5 wt% of water in the feed at 70 °C) carried out before and after all the experiments.

- The membrane is completely inert and it does not influence the reaction kinetics.
- The flux through the membrane, was described using a averaged temperature dependent permeance as explained in Section 3.2. The influence of the concentration of each compound on permeances was considered negligible.
- Constant mixture density was considered.
- Volume change related to the pervaporation was taken into account.

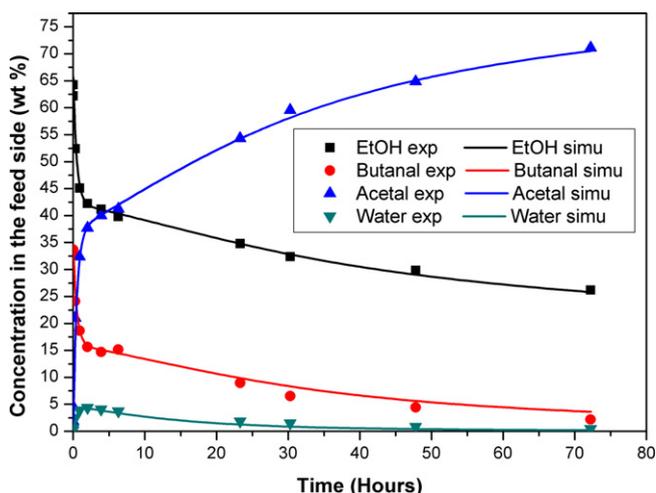
Some authors [43,44] considered that the volume change could be considered negligible and some others took into account this variation [45]. In all these cases the experimental data fit fairly well with the predicted data. HybSi<sup>®</sup> hybrid silica membranes show a relatively high water flux through the membrane compared to other available membranes for similar selectivity values [26,27,29,31]. As a consequence, in the experimental part it was observed that the volume could change around 15%, so this variation was taken into account. The density of the reaction mixture was assumed to be constant since the densities of ethanol, butyraldehyde and 1,1 diethoxy butane at 25 °C are 0.79, 0.803 and 0.82 g/mL respectively. The density of water is 1 but as it is being continuously removed its concentration is low and it does not considerably affect the density in the reaction mixture. This assumption was checked after performing the several simulations by calculating the real reaction mixture density. No significant differences were found: they were smaller than 1%.

The model consists of four molar balances on the feed side, one for each component. Each molar balance was formulated in concentrations and as a result it has three different terms, one related to the reaction rate, one related to the flux through the membrane, and one concerning the effect of the volume change on the concentrations as generated by the pervaporation process. These equations are given in Table 2.

Without any adjustable fit parameter the concentrations of the reaction mixture were predicted and compared to the experimental data. In Fig. 14 we show one representing example. The agreement between experimental and predicted data of the feed concentration profile, in this case and in all other cases, is very good. Only, the amount of butyraldehyde in the reaction mixture is a bit overestimated in the model calculation results, especially at longer reaction times, probably due to the bigger error in the permeance estimation process. These results show clearly the suitability of the current model, and that the assumptions made were justified.

**Table 2**  
Summary of the model equations.

$$\begin{aligned} \text{Mass balance} \\ \frac{d(C_i)}{dt} &= r_i - \frac{J_i A_m}{V_r} - \frac{C_i}{V_r} \frac{dV}{dt} \\ \text{Kinetics} \\ r_i &= v_i \frac{m_{\text{cat}}}{V_r} k_1' C_A^2 C_B - v_i \frac{m_{\text{cat}}}{V_r} k_2' C_C C_D \\ \text{Volume change} \\ \frac{dV_r}{dt} &= -F_p \frac{1}{\rho_r} \quad F_p = \left( \sum_i J_i \right) A_m \frac{MW_p}{10^3} \\ \text{Flux through the membrane} \\ J_i &= Q_0 (\gamma_i x_i P_i^{\text{sat}} - y_i P_i) \quad x_i = \frac{C_i}{\sum_i C_i} \quad y_i = \frac{J_i}{\sum_i J_i} \end{aligned}$$



**Fig. 14.** Feed concentration vs. time and comparison between experimental and simulated data. Conditions: EtOH/butyraldehyde 3:1 ratio, 0.1 wt% catalyst loading, 70 °C, membrane area/reaction volume ratio: 15.1 cm<sup>2</sup>/L.

**4. Conclusions**

By integrating the chemical reaction and the dehydration membrane in one single reactor the equilibrium conversion can be increased from 40% to 70% at 70 °C. At this temperature the water flux through the membrane allows to achieve high conversions faster than at lower temperatures. Still, the relatively small membrane area results in a long reaction time of over 70 h. At this stage, all the water has been removed and further increase in conversion cannot be obtained. To overcome the current experienced limitations of the rate of water removal, optimizations in membrane area, reactor volume and amount of catalyst are needed.

HybSi® membranes can remove selectively water from the ethanol/butyraldehyde/1,1 diethoxy butane/water mixture and are practically impermeable to 1,1 diethoxy butane and butyraldehyde. The current research confirms the high stability of this membrane under demanding conditions and in the presence of aggressive organic solvents, like the aldehyde butyraldehyde. For the first time the mechanical resistance, against a solid catalyst (Amberlyst 47) was proven to be satisfactory. The membrane performance remained essentially constant during the 4 months test period, using only one single membrane tube.

As expected an excess of one of the reactants (ethanol) resulted in a higher final conversion. However, the loss of ethanol through the membrane did increase considerably, when the ethanol:butyraldehyde ratio was increased to 3:1.

The membrane reactor data could be predicted using a model based on independently determined kinetic data for the acetalization reaction and membrane performance, without any adjustable

parameter. This confirms the validity of using temperature dependent averaged permeances for the individual components, and the applicability of this model for preliminary process engineering calculations.

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**Nomenclature**

$A$	pre-exponential factor, (m <sup>3</sup> ) <sup>3</sup> /(mol <sup>2</sup> s kgcat) for forward reaction & (m <sup>3</sup> ) <sup>2</sup> /(mol s kgcat) for reverse reaction
$A_m$	membrane area, m <sup>2</sup>
$C_i$	molar concentration for component i, mol/m <sup>3</sup>
$E_a$	activation energy, J/mol
$F_p$	mass which goes through the membrane, kg/s
$J_i$	Flux through the membrane for component i, mol/(m <sup>2</sup> h)
$k_1'$	kinetic constant for the forward reaction, (m <sup>3</sup> ) <sup>3</sup> /(mol <sup>2</sup> s kgcat)
$k_2'$	kinetic constant for the forward reaction, (m <sup>3</sup> ) <sup>2</sup> /(mol s kgcat)
$m_{\text{cat}}$	catalyst amount, kg
$MW$	average molecular weight of the permeating fluid, kg/mol
$P_{\text{sat},i}$	saturation pressure for component i, bar
$p^{\text{perm}}$	total pressure in the permeate side, bar
$Q_0$	pre-exponential factor for permeances, mol/(m <sup>2</sup> h bar)
$Q_i$	permeance value for component i, mol/(m <sup>2</sup> h bar)
$r_i$	reaction rate for component i, mol/(m <sup>3</sup> s)
$t$	time, s
$T$	temperature, K
$V_r$	reaction volume, m <sup>3</sup>
$W$	catalyst loading, Kgcat/m <sup>3</sup>
$x_i$	liquid molar fraction in the feed mixture
$y_i$	Vapor molar fraction in the permeate mixture
$v_i$	Stoichiometric coefficient for component i
$\rho_r$	Average density of the reaction mixture, kg/m <sup>3</sup>
$\gamma_i$	Activity coefficient for component i

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