Negative impact of butyric acid on butanol recovery by pervaporation with a silicalite-1 membrane from ABE fermentation

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Highlights

- Butanol flux and selectivity suppressed in the presence of butyric acid
- The more butyric acid the poorer the butanol pervaporation
- Mixture pervaporation selectivity strongly affected by adsorption tendency
- High butyric acid concentration and low pH caused nearly 90% butanol flux reduction

Abstract

In this study, the utilization of silicalite-1 membrane pervaporation for butanol recovery from an acetone-butanol-ethanol (ABE) fermentation broth solution was investigated. In particular, the negative effect of butyric acid on the pervaporation performance was tested. The presence of butyric acid was observed to decrease both the butanol flux and selectivity of the membrane. Clear relation between the severity of the decreased performance and the amount of butyric acid was observed. Increasing the pH of the feed solution was observed to improve butanol pervaporation in the presence of butyric acid. In pervaporation of ethanol, butanol and butyric acid, there are significant interactions in adsorption and diffusion between the components. The presence of butanol restricts the permeation of ethanol while the butanol permeation is restricted by the presence of butyric acid. The effects likely arise from adsorptive competition and are further amplified due to the rates of diffusion. In addition, butyric acid exposure may change the membrane properties over time, although they may be restored by heating. The results suggest that the selective recovery of butanol with a silicalite-1 membrane is not feasible if the concentration of butyric acid is significant and the pH value in the solution is low.

Introduction

Butanol (*n*-butanol) can be produced from renewable lignocellulosic biomass through acetone-butanol-ethanol (ABE) fermentation and is a potential biofuel to replace fossil alternatives. Furthermore, compared to well-known biofuel ethanol, butanol has a higher energy content and can be easily blended with petrol [1–3]. The butanol production by ABE fermentation suffers from its low economic sustainability compared to petrochemical processes or to ethanol fermentation [3–6]. For example, the production rate of bioethanol by the fermentation process is 10–30 times higher than that for biobutanol via ABE fermentation [3,6]. Therefore, the main challenges to tackle in ABE fermentation and the subsequent solvent recovery are the low productivity and low concentration of butanol in the broth, mainly due to product inhibition by butanol, and consequently high separation costs.

New separation processes, including organophilic pervaporation, and possibilities for their integration with ABE production are continuously being proposed to decrease the costs of separation that often constitutes a major share of the total process costs, and also to avoid butanol inhibition in order to improve productivity [2,7–12]. Pervaporation and adsorption using organophilic membrane materials are amongst the most attractive methods due to their low energy requirements and potential for high selectivity [13–18]. One such material is MFI-type zeolite analog silicalite-1, which can be used for the selective recovery of butanol by pervaporation from dilute aqueous solutions such as fermentation broths [19,20]. To obtain high purity commercial grade products, distillation is still usually required. However, it is energy intensive. Even using optimized sequence of conventional distillation, the energy requirement is 18.4 MJ kg^{-1} while the energy content of butanol is 36 MJ kg^{-1} [7]. Applying hybrid separation sequences involving membranes can reduce the overall energy costs by half or even more, helping to approach a more commercially viable level [21–23]. For this purpose, silicalite-1 and high silica MFI are interesting membrane materials due to their hydrophobic nature and butanol selectivity [16,24]. Membranes made of silicalite-1 or mixed matrix membranes containing silicalite-1 have been used for the pervaporative separation of butanol with good performance [9,19,25–27].

The fermentative production of butanol via ABE fermentation is possible using many bacterial strains such as strains in the genus *Clostridium* (e.g., *Clostridium acetobutylicum*, *C. beijerinckii*, *C. saccharoperbutylacetonicum*, *C. saccharobutylicum*) and also by using non-*Clostridium*, highly engineered strains (e.g., *Escherichia coli*, *Lactobacillus brevis*, *Pseudomonas putida*, *Lactobacillus buchneri*, *Saccharomyces cerevisiae*) [6]. Using widely available lignocellulosic feedstock is one way to improve the overall sustainability and economy of the production and here the *Clostridium* strains have the advantage of being capable of utilizing both the hexose and pentose sugars originating from lignocellulosic materials [28]. *Clostridium* strains are capable of utilizing both simple and complex carbohydrates, such as glucose, sucrose, and cellulose [29]. In particular, *C. acetobutylicum* and *C. beijerinckii* can produce high yields of solvents, most importantly butanol, ethanol and acetone if appropriate conditions are achieved during fermentation, such as the carbon to nitrogen ratio, pH, and mixture of mineral supplements in the fermentation media [13,30,31].

The fermentation process of solvent-producing C*lostridium* species proceeds through two physiological stages: acidogenesis and solventogenesis [32]. In the initial growth phase, acidogenesis, the cells produce acetic acid and butyric acid in addition to hydrogen and carbon dioxide as their metabolic products. As the pH decreases due to the formation of acidic products, some of the microbial cells shift to the second phase (solventogenesis), during which the carboxylic acids are converted to solvents, i.e. butanol, ethanol, and acetone.

Low production efficiency, leading to high price of the end product, is one disadvantage in butanol production from lignocellulosic biomass by fermentation [3]. Inefficient substrate utilization by bacteria is one reason that causes low rates of the desired solvent product, but also the produced butanol causes inhibition to the bacteria in fermentation media. In fact, even as low as 20 g L^{-1} butanol concentration will cease the cellular metabolism of *Clostridium* [32,33]. The mechanism of butanol toxicity is related to its hydrophobic nature, and the primary effect of this is the disruption of the phospholipid component of the cell membrane [34]. At low concentrations of butanol (< 5 g L^{-1}), no effect on the cell membrane fluidity of *C. acetobutylicum* is detected, but the addition of higher yet subinhibitory concentration of butanol (10 g L^{-1}) causes a 20 to 30 % increase in the fluidity of lipid dispersion of the cell membranes [35]. Thus, the butanol concentration in the broth cannot reach higher levels because of the inhibition effects. *In situ* pervaporation can improve the productivity, the overall concentration, and the sugar conversion significantly [36] and be beneficial for the total energy consumption [8].

Despite the observed potential of pervaporation integrated with ABE production in the literature, the complexity and nonidealities of the broth mixture create issues that may be problematic for the pervaporation performance and operation. The selective separation of the desired component by pervaporation can be disturbed by the unutilized sugars, proteins, and other solvents or metabolic products [19,20,37–40]. Adsorption experiments have shown that carboxylic acids such as acetic acid and butyric acid, which are crucial metabolites in ABE fermentation, easily adsorb onto high silica MFI [16,39,40]. Since silicalite-1 is all-silica MFI analog, this adsorption tendency may also affect the pervaporation performance and cause alcohol flux reduction in silicalite-1 film. The adsorption of carboxylic acids on MFI has been shown to be pH-dependent, and the adsorption selectivity of butanol can be enhanced by increasing the pH [16,41], possibly also improving the overall pervaporation performance.

For feasible process design, it is important to study the factors affecting the selective recovery of butanol by pervaporation. Understanding the mass transfer phenomena and the interaction of permeating components is crucial for the practical design of membrane separation. In this paper, the feasibility of butanol recovery by pervaporation is studied particularly in the presence of butyric acid, which is an inherent component in ABE fermentation and may be present in wide range of concentrations depending on the progress of the fermentation. Butyric acid has been shown in the literature to exhibit higher adsorption tendency to MFI type zeolite compared to e.g. acetic acid that is also an important carboxylic acid intermediate in ABE fermentation [16]. Thus, the butyric acid is seen as the major competitor for butanol in adsorption, and thus further affecting the diffusion of the permeating components and the overall pervaporation performance. Here were study the effect of different butyric acid concentrations on butanol flux and selectivity in pervaporation with silicalite-1 membrane on a ceramic support. The effect of different concentrations of carboxylic acids on butanol pervaporation with an MFI membrane have not been previously reported.

Methods

Microorganism culturing and ABE fermentation

Freeze-stored *C. acetobutylicum* (DSM 1731, DSMZ, Braunschweig, Germany) was activated in RCM media for 14 h [42]. Then, active growing cells (1 mL) were inoculated in 50 mL of sterilized pre-fermentation P2 media prepared in a 125-mL screw-capped bottle. The P2 media contained 30 gL^{-1} glucose and 1 gL^{-1} yeast extract (Becton, Dickinson and Company). Before inoculation, a buffer (50 g L^{-1} KH_2PO_4 (J.T. Baker, Baker analysed), 50 g L^{-1} K_2HPO_4 (J.T.

Baker, Baker analysed), ammonium acetate (220 g L^{-1}) (Merck Pro analysis), minerals (20 g L^{-1} $MgSO_4 \cdot 7H_2O$ (J.T. Baker, Baker analyzed), 1 g L^{1} $MnSO_4 \cdot H_2O$ (Merck Pro analysis), 1 g L^{-1} $FeSO_4 \cdot 7H_2O$ (J.T. Baker, Baker analyzed), 1 g L^{-1} NaCl, and vitamins (0.1 g L^{-1} para-aminobenzoic acid (Sigma), 0.1 g L^{-1} thiamin (ICN), and 0.001 g L^{-1} biotin (Sigma) were added to the P2 media as filter-sterilized stock solutions. The culture was allowed to grow for approximately 16 h at 37 °C before inoculation in the ABE production media.

The fermentation was based on hemicellulose hydrolysate (birch, water extraction at 170 °C, total pretreatment time 90 min). The pretreatment hydrolysate contained monosaccharides: 2.78 g L^{-1} xylose, 2.7 g L^{-1} mannose, 1.17 g L^{-1} galactose, 0.84 g L^{-1} arabinose and 0.62 g L^{-1} glucose. The concentration of oligosaccharidic carbohydrates in the prehydrolysate was analyzed as 16.7 g L^{-1}.

The liquid prehydrolysate was mixed with a heat-treated (121 °C for 20 min) barley grain slurry containing starch at a ratio of 3:2, and this mixture was used as the ABE fermentation media after a pH adjustment to 6.5 with 10 M NaOH. The medium was purged with N_2 to maintain anaerobic conditions and then sterilized (121 °C for 20 min). Before inoculation, filter-sterilized stock solutions of buffer (50 g L^{-1} KH_2PO_4, 50 g L^{-1} K_2HPO_4), and 220 g L^{-1} ammonium acetate, minerals (20 g L^{-1} $MgSO_4 \cdot 7H_2O$, 1 g L^{-1} $MnSO_4 \cdot H_2O$, 1 g L^{-1} $FeSO_4 \cdot 7H_2O$, and 1 g L^{-1} NaCl), and vitamins (0.1 g L^{-1} para-aminobenzoic acid, 0.1 g L^{-1} thiamin, and 0.001 g L^{-1} biotin) were added. Fermentation was started at a media temperature of 37 °C at which the *C. acetobutylicum* DSM 1731 culture (10 %, v/v) was inoculated. Fermentation was stopped after 96 h of incubation and the fermentation broth was stored chilled and filtered to remove solids. The liquid broth was frozen (-18 °C) and defrosted before the pervaporation experiments.

Pervaporation

Pervaporation experiments were performed with two tubular silicalite-1 membranes (A = 0.005 m^2) coated on the inner surface of an α-Al_2O_3 support (Fraunhofer Institute for Ceramic Technologies and Systems). The silicalite-1 layer exhibits MFI pore structure. The Al_2O_3 support consists of four layers, the three interlayers have pores of 100 – 800 nm while the main support layer with 3 mm thickness has pores of 2.3 – 2.5 μm. The membrane thickness was approx. 80 μm. The feed flow was circulated through the tubular membrane at 40 °C at a flow rate of approx. 3 L min^{-1}. This corresponds to a cross flow velocity inside the membrane of approximately 130 cm s^{-1}. According to a Reynolds number analysis in the conditions, the feed flow was turbulent inside the membrane tube. The permeate side was under vacuum ($P_{perm} \leq$ 300 Pa). The permeate was condensed in cold traps submerged in liquid nitrogen. The experimental set-up has been presented in more detail in [43]. The pervaporation samples were analyzed by high performance liquid chromatography (Agilent 1200 series HPLC) using an ICSep ICE-Coregel 87H3 (Transgenomic) column with RI and DA detectors.

Two sets of experiments were done with the silicalite-1 membranes, called M1 and M2. The first set of experiments included experiments with the fermentation broth and synthesized model solutions using membrane M1. The main purposes of the first experimental set were to evaluate the performance of the silicalite-1 membrane using real broth and to make an initial investigation of the effects of alcohols and butyric acid on the performance of the membrane. The aqueous model solutions used as a feed contained either an alcohol and water or a ternary mixture of them or a multicomponent mixture of alcohols, water, and carboxylic acid. The model solutions were prepared by mixing approximately equal molar concentrations of butanol (n-butanol, Merck) and ethanol (ethanol absolute, VWR Chemicals) in water (ultrapure, Milli-Q). In the selected model solutions, acetic acid in form of sodium acetate buffer (0.1 M)

or butyric acid (Acros Organics) was mixed in the solution to evaluate the effect of carboxylic acids on the pervaporation behavior. The sodium acetate buffer solution was done mixing 0.2 M acetic acid solution (acetic acid, glacial (Merck KGaA), and ultrapure water), 0.2 M sodium acetate solution (sodium acetate trihydrate (J.T. Baker), and ultrapure water), and ultrapure water (Milli-Q) in suitable proportions to obtain the desired pH for the buffer solution. In the experiments with butyric acid, the pH level was adjusted with sodium hydroxide to meet the desired pH in the range of 4.5 to 7.8 depending on the experiment. The range of butyric acid addition in the solution varied from 0.2 to 0.8 wt.%. The first set of experiments was performed starting from the real fermentation broth experiment followed by the model solution experiments. The order of the experiments is presented in more detail in the supplementary material. After each pervaporation experiment with membrane M1, a desorption procedure was applied to regenerate the membrane. The procedure consisted of increasing the temperature of the membrane at a rate of 50 °C h^{-1} to 120 °C, while applying vacuum on the permeate side of the membrane and having no feed stream at the feed side. After this, the temperature was kept at 120 °C for over 3 h. High temperature desorption at the same heating rate at max. 220 °C was applied after the first experimental set with model solutions containing butyric acid to ascertain the desorption of the majority of the retained molecules.

The second experimental set with membrane M2 was performed using model solutions to verify the observations with membrane M1 and to broaden the range of experimental conditions. Primarily, the verification was necessary to limit the factors affecting the membrane performance, as the fermentation broth contains multiple compounds that could potentially contribute to changes in permeation behavior. In addition, in the first experimental set, butyric acid was observed as a potentially important factor in the separation. Thus, the second experimental set focused on the effect of butyric acid on the permeation behavior. The concentrations of butanol and water were fixed at 16 and 10 g L^{-1}, respectively, when butyric acid was present in the feed. The separation performance of the membrane was tested with the binary aqueous alcohol solutions and ternary aqueous solutions containing both the alcohols to have an indicator of the separation performance changes over the experimental set. The experiments with butyric acid were started with 1 g L^{-1} butyric acid, which was gradually increased to 4 g L^{-1} while the pH was kept at a low level of 4.5. At butyric acid level of 4 g L^{-1} the pH was adjusted higher to verify the effect of pH. The hypothesis was that by adjusting the pH level to high values, the alcohol separation factor would increase. The fraction of the protonated form of butyric acid should reduce to near zero at high pH values, and thus the readiness of butyric acid adsorption would be decreased. As a result, the sorption of butanol and ethanol would increase in relation to butyric acid and thus their permeation selectivity would increase. In contrast to the first experimental set, no desorption procedure was applied after each experiment in the second experimental set. Instead, the experiments at low pH (4.5) including butyric acid up to 4 g L^{-1} were done in succession, after which a high temperature desorption procedure at 160 °C was applied. Experiments were continued with 4 g L^{-1}at a higher pH of 6-7.7, after which another high temperature desorption procedure was applied where the temperature was raised up to 180 °C. The heating rate was 50 °C h^{-1} and the hold time at the maximum temperature approx. 3 h. Both the experimental sets are presented in chronological order in the supplementary material.

Performance characteristics

The separation performance was evaluated using the flux and separation factor. Flux describes the mass transfer rate of components through the membrane surface area. The steady-state mass flux (J) was determined based on the mass of defrosted permeate sample (m, [kg]), sampling time (t, [h]), and membrane area (A, [m^2]).

$$J = \frac{m}{At}. \quad (1)$$

The separation factor ($\alpha_{i,\mathrm{sol}}$) is a measurement of the selective nature of the pervaporation process for component *i* from the rest of the solution. The separation factor was calculated based on the component mass fractions in the feed and permeate.

$$\alpha_{i,\mathrm{sol}} = \frac{w_{i,\mathrm{perm}}/(1-w_{i,\mathrm{perm}})}{w_{i,\mathrm{feed}}/(1-w_{i,\mathrm{feed}})}, \quad (2)$$

where $w_{i,\mathrm{feed}}$ and $w_{i,\mathrm{perm}}$ are the mass fractions of component *i* on the feed and permeate side of the membrane, respectively.

Results and Discussion

Fermentation broth pervaporation (M1)

The first experimental set was started with pervaporation at 40 °C using real fermentation broth. The experiment results are shown in Table 1. According to the literature concerning high-silica MFI adsorption and pervaporation, a silicalite-1 membrane is assumed to be selective for butanol [16,24]. Instead, the results showed that butanol was not detected in the permeate while the ethanol concentration in the permeate was 8.4 g L^{-1}, which is significantly higher than the feed concentration of 0.6 g L^{-1}. The calculated ethanol separation factor from the solution was high, $\alpha_{\mathrm{EtOH,sol}} = 14$. The total flux continued to decrease from 159 to 34 g m^{-2} h^{-1} during operation, the average flux being 83 g m^{-2} h^{-1}. This indicates that the permeation pathways were being blocked by one or several compounds present in the fermentation broth including e.g. carboxylic acids, proteins, and sugars, which have been observed to disturb selective pervaporation in the literature [19,20,37,40]. Proteins and phenolic compounds have been reported to decrease the alcohol flux [19,20]. Sugar adsorption onto high silica MFI is insignificant but it may alter the flux and separation selectivity by blocking non-zeolitic pathways [20]. In addition, the presence of carboxylic acids may contribute to the reduced flux and selectivity in the pervaporative separation of alcohols [2,3,14,16]. It is noteworthy that the fermentation broth used in this study was produced from a prehydrolysate, which means that the broth also contained furaldehydes (furfural and 5-hydroxymethylfurfural), which also have an affinity to silicalite-1 [44]. On the other hand, the fermentation broth was not used as such but it was first filtered (0.45 μm) to remove any solid particles. The filtered broth liquid was analyzed by high performance liquid chromatography (Agilent 1200 series HPLC). According to the HPLC analysis, the filtered solution that was used in pervaporation contained 0.5 g L^{-1} butanol, 0.6 g L^{-1} ethanol, 1.7 g L^{-1} acetic acid, 1.3 g L^{-1} butyric acid, 0.3 g L^{-1}propionic acid, and 3.2 g L^{-1} glucose. The reported values of carboxylic acids include both the forms of acetic acid and acetate, as well as butyric acid and butyrate or propionic acid and propionate. Acetone was not detected by HPLC in the thawed and filtered broth solution. The concentration of the ABE solvents in the broth was quite low and it is probable that the volatile acetone had escaped from the solution during freezing and thawing, explaining its apparent absence or concentration below the detection limit. In addition, small amounts of other sugars, furfural, and 5-hydroxymethylfurfural were detected in the filtered broth solution. It should be noted that the composition of the broth is strongly dependent on the substrate and microbial strain used, and the stage of the fermentation. Here, the proportion of carboxylic acids in relation to the ABE solvents was quite high. As a reference, a final concentration of 6.7 g L^{-1} butanol, 0.6 g L^{-1} ethanol, 3.4 g L^{-1} acetone, 1.6 g L^{-1} butyric acid and 3.9 g L^{-1} acetic acid was reported when using lignocellulosic hydrolysate supplemented with starchy slurry for ABE production [45]. To give some comparison, the broth used by Oudshoorn *et al*. [46] in their adsorption studies contained 9.02 g L^{-1} butanol, 0.25 g L^{-1} ethanol, 2.33 g L^{-1} acetone, and 0.45 g L^{-1} butyrate,

while the broth used in adsorption studies by Faisal *et al*. [41] contained 2.3 g L^{-1} butanol, 0.36 g L^{-1} ethanol, 0.39 g L^{-1} acetone, 4.35 g L^{-1} butyric acid, and 5.59 g L^{-1} acetic acid. The above-mentioned fermentations were conducted with clostridial strains. The comparison of literature sources regarding ABE fermentations shows that there is a lot of variation in the proportion of the carboxylic acids to the alcohols in the solution. Thus, the significance of the carboxylic acids to membrane separation performance is relevant.

Table 1. Membrane M1 performance with real broth and with synthetic solutions in the absence of carboxylic acids (acetic and butyric acid).

Solution	Feed [g L^{-1}]		Permeate [g L^{-1}]		Flux [g m^{-2} h^{-1}]			$\alpha_{i/\mathrm{sol}}$ [-]	
	Butanol	Ethanol	Butanol	Ethanol	Total	Butanol	Ethanol	Butanol	Ethanol
Real broth [a]	0.5	0.5	0.0 [b]	13.6	36.3	0	0.5		28.6
BuOH	10		81		18.2	1.5		8.7	
BuOH	10		99		15.1	1.5		10.9	
EtOH		9		106	278.2		29.5	-	13.1
BuOH/EtOH	16	9	86	7	27.4	2.4	0.2	5.8	0.8

[a] also contained butyric acid, propionic acid, acetic acid, glucose, hemicellulosic sugars, furfural, HMF, and possibly other fermentation substrate/product compounds.

[b] Butanol was not detected in the permeate with the HPLC configuration having detection limit of butanol concentration approximately <10^{-2} g L^{-1}

Alcohol pervaporation

After the experiment with the real broth, binary alcohol-water pervaporation experiments were performed with the same membrane (M1) to confirm whether the membrane is selective for alcohols, and to explain the reason for the low or even apparently non-existent butanol permeation observed through the membrane. As can be seen in Table 1, pervaporation with an aqueous ethanol solution of 9 g L^{-1} resulted in a separation factor $\alpha_{\mathrm{EtOH/H_2O}} = 13$, and the ethanol concentration in the permeate was 106 g L^{-1}. In turn, using a feed solution of 10 g L^{-1} butanol in water resulted in a permeate butanol concentration of 99 g L^{-1}, yielding $\alpha_{\mathrm{BuOH/H_2O}} = 11$. These binary alcohol/water pervaporations showed that the silicalite-1 membrane is selective for alcohol as expected and can generally be used to recover alcohols from an aqueous solution. It is also noteworthy that the flux of ethanol from a binary solution is significantly higher than that of butanol.

In contrast, when the feed solution contained both butanol and ethanol in addition to water, the ethanol flux was significantly reduced, and ethanol was not concentrated in the permeate, as shown in Table 1. The main reason for this is probably the preferred sorption of butanol on an MFI-type zeolite as it is a more hydrophobic alcohol than ethanol [16]. In addition, ethanol diffusion in the zeolite pores is slowed down by the presence of the slower butanol. Likewise, it could be speculated that the butanol flux could be improved by the faster-diffusing ethanol, effect which has been observed in molecular simulations [47]. In the present pervaporation experiments it is not possible to separate the effect of adsorption and diffusion and the presence of this effect cannot be verified. Nevertheless, the results imply that the presence of ethanol in the fermentation broth neither significantly decreases nor increases the permeation rate of butanol through the silicalite-1 membrane, while the presence of butanol restricts ethanol adsorption and permeation.

Effect of carboxylic acids

The first experimental set was continued by investigating the effect of carboxylic acids on the membrane behavior. The fermentation broth contained both acetic acid (1.7 g L^{-1}) and butyric acid (1.3 g L^{-1}) in appreciable amounts. The presence of carboxylic acids is often linked to both decreased alcohol selectivity and flux reductions in the pervaporative separation of alcohols [19,20,37,40]. For example, Bowen *et al.* (2007) [40] suggested that acetic acid competes for the adsorption sites in a ZSM-5 zeolite-filled polydimethylsiloxane membrane with ethanol and water, thus reducing the performance of the membrane. Additionally, the acetate groups of otherwise attached acetic acid molecules near the pore openings of the zeolite may inhibit the transport of ethanol through zeolite particles [40]. It has also been suggested that carboxylic acids interact with silanol groups and make the membrane more hydrophilic [37,40]. Thus, the carboxylic acids are also likely to have significance in the permeation behavior of butanol and ethanol. To investigate this, experiments were performed using solutions of aqueous butanol and ethanol with acetate buffer and acetate buffer mixed with butyric acid. An 0.1 M acetate buffer was used to adjust the pH to the desired level and to provide acetic acid. The molar extent of the alcohols in the model solutions was roughly equal. The results in presence of the carboxylic acids are shown in Table 2 and compared with the results from experiments with the real broth and alcohol-water solution.

Table 2. Permeation in presence of acetic and butyric acid.

Experiment	Feed concentrations [g L^{-1}]					Flux [g m^{-2} h^{-1}]			Permeance of butanol/ permeance of ethanol [d]
	Butanol	Ethanol	Butyric acid [a]	Acetic acid [b]	pH	Total	Butanol	Ethanol	
Broth[c]	0.5	0.6	1.3	1.7	4.5	83.4	0	0.70	
BuOH/EtOH	16	9			~6	27.4	2.4	0.2	15
BuOH/EtOH/AA	3.3	2.0		5.9(2.3)	4.6	32.0	1.26	0.10	16
BuOH/EtOH/AA/BA	4.7	3.1	2.8	7.8(2.0)	4.7	31.5	0.29	0.09	5

[a] Value of both butyric acid and butyrate.

[b] Value of both acetic acid and acetate. Sources of acetate were sodium acetate and acetic acid. The part of the acetic acid in the model solutions is given in parentheses.

[c] Real broth also contains glucose, hemicellulosic sugars, furfural, HMF, and possibly other fermentation substrate/product compounds.

[d] Permeance [mol $m^{-2}h^{-1}Pa^{-1}$].

As shown in Table 2, the selectivity of the membrane for butanol or ethanol is not significantly affected by the presence of acetic acid in the feed solution. In the presence of acetic acid, the butanol flux is significantly higher than the flux of ethanol, and the results show no decrease in the relative flux or the separation factor. In fact, the calculated separation factors of both butanol ($\alpha_{\mathrm{BuOH/sol}} = 12.4$) and ethanol ($\alpha_{\mathrm{EtOH/sol}} = 1.6$) were higher than in the reference case of aqueous butanol/ethanol solution ($\alpha_{\mathrm{BuOH/sol}} = 5.8$, $\alpha_{\mathrm{EtOH/sol}} = 0.8$). In contrast, in the presence of acetate buffer and butyric acid, butanol flux and membrane selectivity decrease considerably in relation to the results observed in the alcohol/water solution experiment; with the butanol separation factor decreasing to 2. These results imply that acetic acid cannot be regarded as the reason for the non-existent flux of butanol from the fermentation broth, whereas butyric acid seems a potential candidate for this.

Effect of butyric acid

The effect of the butyric acid concentration level and the pH were evaluated using a series of experiments with varying butyric acid concentrations using membrane M1 in the pervaporation experiments. According to the literature, the adsorption tendency of butyric acid on MFI type zeolite is even higher than that of butanol [16,39,46], which most likely affects also the pervaporation. However, as shown by Ikegami *et al*. [39] and Faisal *et al*. [16], increasing the pH decreases butyric acid adsorption. The reason for this is that the protonated form of butyric acid, which is dominant at low pH values (below pKa 4.8), has a higher affinity for the hydrophobic MFI zeolite compared to the deprotonated form [16,39,41]. This is further explained by the hydrophobicity of the molecules, as the protonated form is less polar than the deprotonated one [16,39,41]. Butyric acid can thus affect butanol adsorption and, if the molecules compete on the same adsorption sites, the effect may be amplified at low pH. To investigate this more closely, several experiments were performed with feed solutions of varying butyric acid concentrations and pH. These experiments were compared with the pervaporation experiment with the real broth and experiments in the absence of butyric acid. The results of these experiments are presented in Table 3.

Table 3. Aqueous butanol/ethanol/butyric acid experiments with membrane M1. (pK_a=4.8 for butyric acid)

Feed concentrations g L^{-1}			pH[a]	Flux g m^{-2} h^{-1}			Permeance of butanol/ permeance of ethanol [c]
Butanol	Ethanol	Butyric acid		Total	Butanol	Ethanol	
16	9			27.4	2.35	0.19	15
15	12	2	7.5	36.4	1.54	0.30	9
15	11	8	7.8	27.2	0.77	0.13	9
13	12	5	7.7	39.6	0.67	0.15	9
14	10	5	5.5	35.1	0.35	0.21	3
14	11	5	4.5	37.4	0.28	0.26	2
2	3	9	4.6	21.0	0.002	0.008	0.3
2	3	4	4.6	38.6	0.08	0.03	4
10				15.1	1.49		
	9			278.3		29.49	
0.5 [b]	0.6 [b]	1 [b]		36.3	0	0.208	

[a] pH adjusted with NaOH before PV when butyric acid was present (except for real broth).
[b] broth also contained other components.
[c] Permeance [mol $m^{-2}h^{-1}Pa^{-1}$].

As can be seen in Table 3, the presence of butyric acid was observed to restrict the butanol flux, whereas the flux of ethanol remained relatively constant, although at a low level. The ethanol flux was comparable to the level observed with the ternary butanol/ethanol/water mixture. The flux of butanol in the absence of butyric acid from the ternary butanol/ethanol/water mixture was 2.4 g m^{-2} h^{-1}, while the flux of ethanol was 0.19 g m^{-2} h^{-1}. When a feed solution containing butanol, ethanol, and butyric acid in water was applied in the same 40 °C pervaporation conditions, the ethanol flux was 0.13 – 0.30 g m^{-2} h^{-1}. This is roughly the same as in the absence of butyric acid. In contrast, the butanol flux was drastically affected by the addition of butyric acid. The effect of butyric acid on the butanol flux was the most prominent at low pH values, as expected according to the sorption data of Ikegami *et al*. [39] and Faisal *et al*. [16,41]. At

low pH values, the majority of the butyric acid is in the protonated form, which has a higher affinity for high silica MFI compared to the deprotonated form [16,39]. At pH 4.5, the butanol flux was 0.28 g m^{-2} h^{-1}, i.e., approximately 12% of the flux (2.4 g m^{-2} h^{-1}) observed without butyric acid in the feed solution. Even though a pH increase is beneficial for the butanol adsorption and flux due to the decreased competition with butyric acid of the sorption sites, the presence of butyric acid even at small concentrations appears to disturb the butanol permeation. In conditions with a low butyric acid feed concentration of 2 g L^{-1} and elevated pH of 7.5, the butanol flux was 1.54 g m^{-2} h^{-1}, which is still one third short of the reference level in the absence of butyric acid.

Verification of the effect of butyric acid (M2)

The first experimental set results described above imply that the extremely low selectivity of the membrane for butanol with real broth is caused by the presence of butyric acid, and that the effect is more drastic at low broth pH due to the higher amount of the protonated form of butyric acid. However, it is noteworthy that the first experiment in the first experimental set was done with the fermentation broth. Thus, the subsequent experiment results may have been compromised as the membrane characteristics may have in fact changed due to the contact with the other components in the fermentation broth that could potentially have affected the permeation behavior, e.g., proteins and sugars [19,20]. Therefore, the effect of butyric acid was investigated with the second experimental set, which was performed using the fresh silicalite-1 membrane M2. Table 4 shows the results using membrane M2.

Table 4. Aqueous butanol/ethanol/butyric acid experiments with membrane M2. (pK_a=4.8 for butyric acid)

Feed concentrations [g L^{-1}]			pH [a]	Flux [g m^{-2} h^{-1}]			Permeance of butanol/ permeance of ethanol [b]
Butanol	Ethanol	Butyric acid		Total	Butanol	Ethanol	
16	10		6	119	4.6	1.2	5.4
16	10	1	4.7	77.6	1.8	0.7	3.6
16	10	1.5	4.6	71.6	1.5	0.6	3.3
16	10	2	4.6	70.6	1.4	0.6	3.0
16	10	4	4.5	62.8	0.6	0.4	2.3
16	10	4	6	65.9	1	0.5	2.6
16	10	4	7.6	41.9	1.5	0.3	6.7
16	10	4	6.3	43.2	1	0.3	4.3
16				169.2	4.8		
	10			1636.2		122.5	

[a] pH adjusted with sodium hydroxide when butyric acid was present
[b] Permeance [mol $m^{-2}h^{-1}Pa^{-1}$].

Table 4 shows that the butanol flux in reference conditions without butyric acid is 4.6 g m^{-2} h^{-1}, and at pH 4.5 and high butyric acid concentration of 4 g L^{-1}, the butanol flux is only 0.6 g m^{-2} h^{-1}, corresponding to 87% reduction of butanol flux. Also, the separation factor of butanol, $\alpha_{\mathrm{BuOH,sol}}$, in these conditions is decreased below unity, to value 0.6 from the initial value of 2.5. Comparison of Tables 3 and 4 shows that the fluxes using membrane M2 are in general greater than with

membrane M1 in corresponding experiments. This may indicate that the active surface area of membrane M1 was blocked due to the exposure to the fermentation broth compounds. However, membrane M1 seems to be more selective for butanol over ethanol than membrane M2, which in turn has higher fluxes. This implies that the proportion of defects may be larger in M2 than in M1. Fig. 1 shows how the butanol separation factor changes in different conditions in presence of butyric acid.

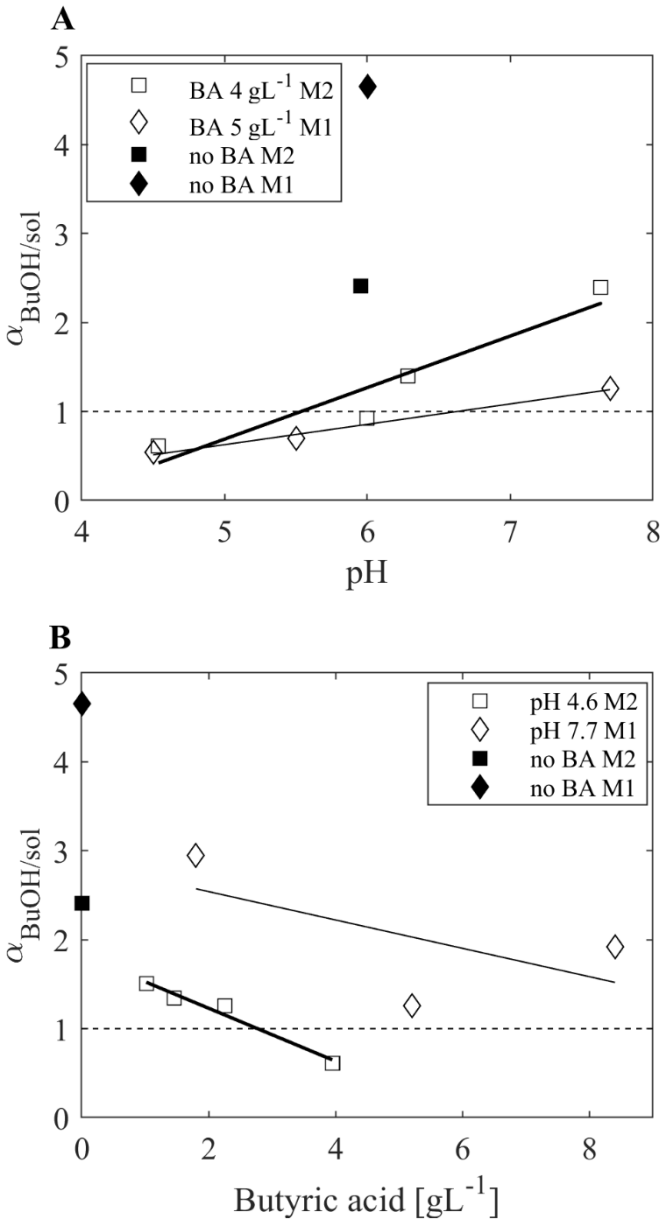

Figure 1. The separation factor of butanol from solution **A**) in the presence of butyric acid in the feed at an average concentration of 5 g L^{-1} (M1) (open diamond) or 4 g L^{-1} (M2) butyric acid (open square) at different pH levels, and **B**) at high pH (M1, average pH 7.7) or at low pH (M2, average pH 4.6) when the butyric acid feed concentration is altered. The reference state without butyric acid is shown with corresponding black markers. The linear trends are shown with solid lines (thin line for M1 and thick line for M2). $\boldsymbol{\alpha_{BuOH/sol} = 1}$ is indicated by the dashed line for guidance.

As shown in Fig 1a, an increase in the pH results in the increase of the separation factor of butanol with both membranes. It is noted that the separation factors even in the absence of butyric acid are relatively low, and literature has many membranes with better butanol separation performance (see also supplementary Material Table S4), but the trends observed here as the function of pH and butyric acid concentration are clear and consistent. At low pH, the separation factor of butanol decreases so drastically that the separation factor $\alpha_{\mathrm{BuOH,sol}}$ is less than unity. The ethanol separation factor, not presented in Fig. 1, was below unity when butanol was present in the solution, regardless of the changes in the other parameters of the experimental conditions. It is worth noting that the butanol separation factor at high pH (7.6) was at a comparable level to the value observed in the absence of butyric acid when using membrane M2. This supports the assumption that the high affinity of butyric acid especially in its protonated form, blocks the adsorption of butanol. Furthermore, the separation factor of butanol is also better when the amount of butyric acid is low, as shown in Fig. 1b. The dependence of butanol flux on the conditions is in turn illustrated in Fig. 2. The experiments included in Figs. 1a and 2a were conducted at a constant butyric acid feed concentration of 4 g L^{-1} with membrane M2, and 5 g L^{-1} with membrane M1. Correspondingly, Figs. 1b and 2b include experiments at an average pH of 4.6 using membrane M2 and an average pH of 7.7 using membrane M1. In addition, the butanol and ethanol concentrations were fixed.

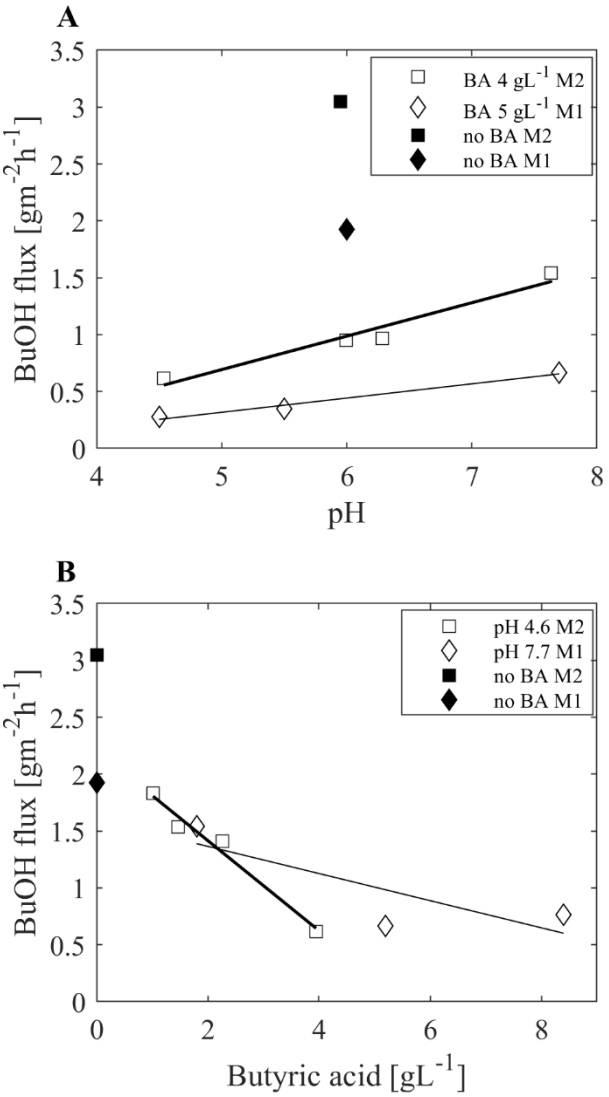

Figure 2. The flux of butanol **A)** in the presence of butyric acid at a feed concentration of 5 g L^{-1} (M1) (open diamond) or 4 g L^{-1} (M2) (open square) at different pH levels, and **B)** at high pH (M1, average pH 7.7) or at low pH (M2, average pH 4.6) at different butyric acid concentrations. The reference state without butyric acid is shown with closed markers. The linear trend lines are shown with solid lines (thin line for M1 and thick line for M2).

The observed trends in Fig. 2 are similar to those in Fig. 1. As can be seen in Fig. 2a, the flux of butanol increases steadily as the pH is increased. On the other hand, it can be seen in Fig 2b that at a low pH of 4.5 there is a steep decrease in the butanol flux through membrane M2 as the concentration of butyric acid in the feed solution is increased. A similar, but not as steep-sloping, effect was observed at elevated pH using membrane M1. Fig. 2a shows that there is a clear linear relation between the pH and butanol flux: The lower the pH, the lower the butanol flux. Thus, pH elevation appears to be beneficial for butanol recovery by pervaporation in the presence of butyric acid as both the butanol flux and butanol separation factor are higher.

However, interestingly, the ethanol flux is not significantly affected by the addition of butyric acid, as shown in Tables 3 and 4. On the other hand, it can be stated that, in general, the butanol flux is higher than the flux of ethanol. However, the butanol flux decreases as the concentration

of butyric acid is increased. At low pH, when there is a reasonably large amount of butyric acid, particularly in protonated from, the fluxes of butanol and ethanol are at a comparable level. For example, in the case of membrane M2, at pH 4.5 and a butyric acid feed concentration of 4 g L^{-1}, the fluxes of butanol and ethanol were 0.6 g m^{-2} h^{-1} and 0.4 g m^{-2} h^{-1}, respectively. Based on the trends, the selectivity between the two alcohols could turn around if the presence of the protonated form of butyric acid was further increased either by reducing the pH or introducing a higher concentration of butyric acid. An additional experiment with membrane M1 using a feed solution containing 3.4 g L^{-1} butanol, 2.2 g L^{-1} ethanol, and 9.2 g L^{-1} butyric acid at pH 4.6 resulted in the inverted selectivity of butanol and ethanol, i.e., the permeate contained more ethanol than butanol. On the other hand, all the organic fluxes were extremely low. In the absence of butyric acid, the selectivity for butanol over ethanol is significantly higher. Interestingly, the data (see Tables 3-4) shows that the ethanol flux is slightly enhanced at low pH, in which conditions the butanol flux is most restricted. It is possible that the significant suppression of butanol adsorption due to competition with butyric acid results in a higher ethanol flux. This would suggest that there are adsorption sites available for ethanol that are not available for butanol adsorption. Molecular simulations have shown that the preferred adsorption site of ethanol in silicalite is located in the zig-zag channels and then in the channel intersections [47,48]. Butanol is a larger molecule, which may restrict its adsorption on certain sites. The length of the molecules generally affects the preferred adsorption sites, with larger ones locating in straight channels while smaller molecules fill the zig-zag channels [49]. As a whole, the results suggest that the presence of components such as proteins and sugars in the fermentation broth in the first experimental set (with M1) did not cause the low selectivity of the membrane, but rather the effect is linked to the concentration of butyric acid and pH of the fermentation broth. Furthermore, these observations indicate that the behavior can be deduced to originate from adsorption phenomena. Butanol and butyric acid are shown to exhibit high affinity to high silica MFI [16,39,41,46], thus potentially suppressing the adsorption of ethanol on silicalite-1, which is the all-silica MFI. The negative effect of butyric acid on butanol flux is reduced with increasing pH, as a high proportion of the acid dissociates in these conditions (pK_a 4.8 for butyric acid) [16,40,41] (Fig. 2b).

Moreover, despite the preferential adsorption of butyric acid, the concentration of butyric acid could not be quantified in the permeate in any of the experiments in the two experimental sets until after a long exposure time, indicating that the diffusion of butyric acid in silicalite-1 pores is very slow. This can be attributed both to the strong sorption of butyric acid to the adsorption sites and the large molecular size of butyric acid in relation to the zeolite pore size resulting in size exclusion effects. In addition, if a butyric acid molecule occupies a site near a zeolite pore opening, it may physically block the permeation of ethanol and butanol through the zeolitic pores [40]. This kind of effect was assumed by Bowen *et al*. [40], as they suggested that acetate groups of acetic acid molecules near the zeolite pore opening could inhibit ethanol transport through the zeolite in pervaporation using MFI-filled PDMS. In addition, the adsorption of carboxylic acids may make the surface of the membrane more hydrophilic [39,50], thus decreasing the selectivity toward alcohols, also allowing a higher water flux in relation to the organic flux.

Membrane performance

Due to the strong sorption affinity of butyric acid on zeolite and its slow diffusion in the zeolite pores, some butyric acid molecules are likely to remain sorbed on the silicalite-1 after the membrane was exposed to the butyric acid during the experiments. Therefore, desorption procedures at elevated temperatures were used to desorb butyric acid after the set of

experiments, as described in the Methods section. The success of the desorption procedure was evaluated using the maximum quantity of butyric acid sorbed on the zeolite film.

The theoretical maximum quantity of butyric acid sorbed was estimated using literature knowledge of butyric acid saturation loadings on a high silica MFI adsorbent of 0.025 g g^{-1} or 0.13 g g^{-1}, at pH 6 and pH 4, respectively [16,46]. In addition, it was approximated that the silicalite-1 film volume was 0.38 cm^3. The density of silicalite-1 is 1.763 g cm^{-3} [51]. Thus, combining this knowledge resulted in a maximum value of 16 – 86 mg butyric acid sorbed on the silicalite-1 film, depending on the pH of the solution.

In the first case of the experimental set using membrane M1, the desorption procedure was performed by increasing the membrane temperature up to 120 °C. During the desorption procedures after experiments containing 4 or 9 g L^{-1} butyric acid at low pH 4.6, a total of approximately 24 mg or 37 mg of butyric acid, respectively, was collected as permeate. The collected amount of butyric acid fits within the range calculated for the theoretical maximum sorbed amount of butyric acid. Thus, it was assumed that at least the majority of the butyric acid was mobilized from the adsorption sites during the temperature elevation to 120 °C and therefore the adsorbed compounds should not have interfered with the subsequent experiments. However, the first experimental set with membrane M1 was finished with experiments using solutions containing butanol, ethanol, and water, i.e., no butyric acid. After these experiments a high temperature desorption procedure was applied with a maximum temperature of 220 °C. The sample collected during the desorption procedure contained 2 mg ethanol, 13 mg butanol, and 3 mg butyric acid. Most of the butanol was detected in the samples collected at temperatures around 160 ° C, i.e., during heating from 120 to 160 °C and subsequently from 160 to 220 °C, which is in line with the desorption temperatures presented by Faisal *et al.* [16] for high-silica MFI. However, most of the butyric acid was collected while heating up from 160 to 220 °C and cooling back to 160 from 220 °C, indicating that butyric acid requires even more efficient desorption procedures than butanol. It can be stated that some butyric acid remained in the membrane despite the fact that the normal desorption procedure at 120 °C was applied after each experiment.

In the second experimental set with membrane M2, desorption at 160°C was applied after experiments at low pH (4.5) including butyric acid up to 4 g L^{-1}. Another high temperature desorption procedure where the temperature was increased up to 180 °C was applied after the experiments that were performed with 4 g L^{-1} butyric acid at elevated pH values of 6 – 7.7. In both desorptions, the highest amount of butanol was recovered during heating between the temperatures of 120 – 160 °C, while the highest amount of butyric acid was collected during maintaining the temperature at 160 °C. At temperatures higher than 160 °C no more permeate was collected. Based on the amounts recovered during the desorption procedure, it was calculated that the membrane loading was 0.11 – 0.14 g g^{-1} for butanol and 0.004 –0.02 g g^{-1} for butyric acid after experiments at high or low pH, respectively. Butanol saturation loading is reported to be between 0.0854 and 0.12 g g^{-1} [16,46,52] while butyric acid saturation loading is reported to be 0.025 gg^{-1} at pH 6 or 0.13 gg^{-1} at pH 4 [16,46].The range of the calculated butanol loadings based on desorbed amounts is close the saturation loading. The desorbed amount of butyric acid corresponds quite well to the lower literature value of saturation loading at high pH. It should be noted that these loadings are only rough estimates, based on the amount of the components obtained in cold traps during desorption and approximation of silicalite-1 mass, and should be regarded merely as indicative of the efficiency of the applied desorption procedures in mobilizing the remaining sorbed components from the membrane to the permeate side. However, it can be assumed that the membrane is regenerated by this procedure. The theoretical comparison of the adsorption loadings supports the assumption that butyric acid is strongly adsorbed on the silicalite-1 film and its diffusion is slow. The strong adsorption of

butyric acid, and its slow diffusion, which is partly due to its large size, are likely to block the adsorption of butanol as butyric acid is occupying the adsorption sites. Furthermore, adsorption of butyric acid could possibly enhance water adsorption due to the hydrogen bonding tendency of the carboxyl group. Ikegami *et al.* [39] suggested that the adsorption of butyric acid occurs through an aliphatic chain leaving the carboxyl group available for interaction with water, for example.

Although at least the majority of butyric acid was desorbed from the silicalite-1, the reference experiments without butyric acid using solution of butanol/ethanol/water showed a decrease in flux over time. (For more details, see experimental summary in the supplementary material, Table S1 and Table S2.) This implies that there occurred some changes in membrane properties as a result of the characteristics of the solutions, conditions, and duration of the experiments. As an example, any remaining butyric acid may gradually block the membrane adsorption sites thus decreasing the membrane performance. On the other hand, performance is regenerable at least to some degree. For example, in the first experimental set with M1, the initial fluxes of butanol and ethanol were 2.35 g m^{-2} h^{-1} and 0.19 g m^{-2} h^{-1}, respectively. In contrast, pervaporation with a solution of butanol/ethanol/water immediately after the experiments including butyric acid resulted in butanol and ethanol fluxes as low as 0.27 g m^{-2} h^{-1} and 0.24 g m^{-2} h^{-1}, respectively. These were roughly equal to the preceding experiment with 5 g L^{-1} butyric acid at pH 4.5. After the high temperature desorption that was applied to restore membrane performance, the butanol flux was improved to 1.35 g m^{-2} h^{-1}, while the ethanol flux remained at 0.24 g m^{-2} h^{-1}. Application of the high temperature desorption procedure resulted in the partial regeneration of the butanol flux, presumably by evicting the adsorbed species, butyric acid in particular. A temperature increase is thus a possible way to regenerate the performance of non-polymeric membranes. Washing and soaking of the membrane surface with water or aqueous alcohol solutions can also be used to regenerate deteriorated membranes after exposure to ABE broths [20].

Membrane deterioration may also occur through other mechanisms. It has been suggested that weak acids may make a hydrophobic membrane more hydrophilic by interacting with silanol (Si-OH) groups [37,40]. In general, the hydrophobic nature of zeolite membranes is caused by the presence of ≡Si–O–Si≡ –bonds in the zeolite, resulting in a lack of ionic sites for water adsorption. The ≡Si–O–Si≡ –bonds can be broken, for example because of the interaction with weak acids and as a result the surface will have silanol groups. This in turn decreases the hydrophobicity of the zeolite. Extra-framework cations and silanol groups are two of the main defect types increasing the water adsorption potential [53].

It is probable that alteration of the silicalite-1 membrane properties and membrane deterioration to some degree occur due to contact with the components in a fermentation broth. If there occurs deterioration, it may cause problems in long-term operation. The potential structural changes and membrane characteristics alteration were evaluated using x-ray diffraction (Rigaku SmartLab XRD, Centre of Material Analysis, University of Oulu) and nitrogen adsorption methods (ASAP2020, Micromeritics, Environmental and Chemical Engineering, University of Oulu). The potential changes in the membrane characteristics could not be quantitatively or qualitatively verified with the selected methods. Uncertainties brought mainly due to the high fraction of the alumina support compared to the fraction silicalite-1 in the analyzed membrane samples also affected the success of the analyses. The analyses are described in supplementary material. However, the results presented here still show a clear response to changes in process conditions, indicating that possible membrane alteration does not have any significant effect on the pervaporation characteristics throughout the experiments, and that the trends presented for membrane performance in the presence of butyric acid are indeed credible. A graphical

presentation of the performance and the changes in process conditions such as pH and butyric acid concentration can be found in the supplementary material (Figure S1).

The silicalite-1 membrane may be selective to butanol from binary aqueous solution, but the performance is affected by other solvents in the solution in multicomponent pervaporation. Thus, the effect of butyric acid should not be ignored in design of novel butanol recovery methods applying pervaporation. In industrial scale, stable operation is important. Since pervaporation has shown its potential to selectively recover organic solvents such as bio-alcohols even from low concentration solutions, the future process design will benefit from the knowledge how different conditions may disturb the process. The effect of butyric acid on butanol recovery with silicalite-1 seems to be clear: the higher the butyric acid concentration and the lower the pH, the poorer the pervaporative recovery of butanol. On the other hand, ethanol cannot be recovered by this type of membrane in the presence of butanol. Even though the fluxes and separation factors of the silicalite-1 membrane used in this work were relatively low compared to the observed butanol selectivities or fluxes presented in literature [9,19,24–27], similar negative effect of butyric acid as observed here is likely to occur also in better-performing membranes of MFI type, or in membranes containing silicalite-1 particles. We suggest that the observed effects are mainly due to the differences in the adsorption affinities of the compounds, but further studies on the diffusivity of the carboxylic acids and alcohols by molecular simulation, for example, could give better understanding of all the phenomena. The understanding could help to predict the performance of the separation processes, benefitting the process design in these applications.

Conclusions

It was observed that both the butanol flux through the silicalite-1 membrane and the membrane selectivity for alcohols were reduced in the presence of butyric acid. The magnitudes of the effects were proportional to the amount of butyric acid and pH: significantly poorer performance was observed at lower pH and at higher butyric acid concentration. It can be also concluded that significant interactions were observed in the adsorption and diffusion behavior of mixtures containing alcohols and carboxylic acids.

Silicalite-1 shows significant selectivity for both ethanol and butanol from binary aqueous solutions. When both ethanol and butanol are present in the solution, the flux of ethanol is significantly suppressed, and silicalite-1 thus shows higher selectivity for butanol over ethanol.

In contrary, the butanol flux was strongly suppressed in the pervaporation experiments with the real fermentation broth that contained high concentrations of acetic and butyric acids. Experiments using alcohol-water solutions with either acetic acid or butyric acid showed that the presence of acetic acid had insignificant effect to the butanol pervaporation. Instead, the butanol flux was significantly suppressed in the presence of butyric acid in the solution with clear trend: the higher the butyric acid concentration, the worse the butanol flux. Also, the lower the pH and thus the higher the concentration of the protonated form of the butyric acid, the lower the butanol flux.

A probable cause for this disrupting effect of butyric acid is its high tendency to adsorb on the surface of a silicalite-1 film. In addition, butyric acid diffusion within the zeolite pores appears to be slower than that of butanol and ethanol. As a result, butyric acid occupies the majority of the sorption sites on the silicalite-1 and subsequently also blocks the diffusion of butanol and ethanol within the zeolite pores. The observed effects between butyric acid, butanol and ethanol

are likely largely due to the preferred adsorption tendency of the compounds on silicalite-1 in decreasing order: butyric acid, butanol, and ethanol.

Thus, selective recovery of butanol with a silicalite-1 membrane may not be feasible if the concentration of the carboxylic acids, especially butyric acid, is significant and the pH in the solution is low. Here, almost 90 % reduction of butanol flux was observed at conditions with high concentration of butyric acid and low pH. Similar negative effect is probable also in the case of higher performance membranes.

The effect caused by butyric acid is at least partly reversible by removing adsorbed species from the membrane. However, the experiments and available analysis methods could not exclude, nor verify, if there occurs any permanent damage to the membrane due to the exposure to carboxylic acids.

The effect of carboxylic acids and other components on the membrane-assisted recovery process should be taken into consideration when designing processes that apply novel recovery methods for bioalcohols. The results obtained here give insight to the effects that can be present in presence of reasonable concentrations of carboxylic acids, especially butyric acid in the recovery of butanol by pervaporation using a hydrophobic zeolite membrane.

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References

[1] M. Kumar, K. Gayen, Developments in biobutanol production: New insights, Appl. Energy. 88 (2011) 1999–2012. doi:10.1016/J.APENERGY.2010.12.055.

[2] A. Kujawska, J. Kujawski, M. Bryjak, W. Kujawski, ABE fermentation products recovery methods—A review, Renew. Sustain. Energy Rev. 48 (2015) 648–661. doi:10.1016/J.RSER.2015.04.028.

[3] C. Jin, M. Yao, H. Liu, C.F. Lee, J. Ji, Progress in the production and application of n-butanol as a biofuel, Renew. Sustain. Energy Rev. 15 (2011) 4080–4106. doi:10.1016/J.RSER.2011.06.001.

[4] C. Xue, J.-B. Zhao, L.-J. Chen, F.-W. Bai, S.-T. Yang, J.-X. Sun, Integrated butanol recovery for an advanced biofuel: current state and prospects, Appl. Microbiol. Biotechnol. 98 (2014) 3463–3474. doi:10.1007/s00253-014-5561-6.

[5] C. Xue, X.-Q. Zhao, C.-G. Liu, L.-J. Chen, F.-W. Bai, Prospective and development of butanol as an advanced biofuel, Biotechnol. Adv. 31 (2013) 1575–1584. doi:10.1016/J.BIOTECHADV.2013.08.004.

[6] Y. Li, W. Tang, Y. Chen, J. Liu, C.F. Lee, Potential of acetone-butanol-ethanol (ABE) as a biofuel, Fuel. 242 (2019) 673–686. doi:10.1016/J.FUEL.2019.01.063.

[7] K. Kraemer, A. Harwardt, R. Bronneberg, W. Marquardt, Separation of butanol from acetone–butanol–ethanol fermentation by a hybrid extraction–distillation process, Comput. Chem. Eng. 35 (2011) 949–963. doi:10.1016/J.COMPCHEMENG.2011.01.028.

[8] D. Cai, S. Hu, Q. Miao, C. Chen, H. Chen, C. Zhang, P. Li, P. Qin, T. Tan, Two-stage pervaporation process for effective in situ removal acetone-butanol-ethanol from fermentation broth, Bioresour. Technol. 224 (2017) 380–388. doi://doi.org/10.1016/j.biortech.2016.11.010.

[9] J. Li, X. Chen, B. Qi, J. Luo, X. Zhuang, Y. Su, Y. Wan, Continuous Acetone–Butanol–Ethanol (ABE) Fermentation with in Situ Solvent Recovery by Silicalite-1 Filled PDMS/PAN Composite Membrane, Energy & Fuels. 28 (2014) 555–562. doi:10.1021/ef401706k.

[10] M. Stoller, M. Bravi, P. Russo, Development of a Process for N-butanol Recovery from Abe Wastewater Streams by Membrane Technology, Chem. Eng. Trans. 74 (2019) 937-942 SE-Research Articles. doi:10.3303/CET1974157.

[11] C. Bildea, I. Patraşcu, J.G. Hernandez, A. Kiss, Enhanced Down-Stream Processing of Biobutanol in the ABE Fermentation Process, in: Comput. Aided Chem. Eng., 2016: pp. 979–984. doi:10.1016/B978-0-444-63428-3.50168-5.

[12] G. Liu, W. Wei, W. Jin, Pervaporation membranes for biobutanol production, ACS Sustain. Chem. Eng. 2 (2014) 546–560. doi:10.1021/sc400372d.

[13] T.C. Ezeji, N. Qureshi, H.P. Blaschek, Butanol fermentation research: upstream and downstream manipulations, Chem. Rec. 4 (2004) 305–314. doi:10.1002/tcr.20023.

[14] V. García, J. Päkkilä, H. Ojamo, E. Muurinen, R.L. Keiski, Challenges in biobutanol

production: How to improve the efficiency?, Renew. Sustain. Energy Rev. 15 (2011) 964–980. doi:10.1016/J.RSER.2010.11.008.

[15] A. Oudshoorn, L.A.M. van der Wielen, A.J.J. Straathof, Assessment of Options for Selective 1-Butanol Recovery from Aqueous Solution, Ind. Eng. Chem. Res. 48 (2009) 7325–7336. doi:10.1021/ie900537w.

[16] A. Faisal, A. Zarebska, P. Saremi, D. Korelskiy, L. Ohlin, U. Rova, J. Hedlund, M. Grahn, MFI zeolite as adsorbent for selective recovery of hydrocarbons from ABE fermentation broths, Adsorption. 20 (2014) 465–470. doi:10.1007/s10450-013-9576-6.

[17] H.-J. Huang, S. Ramaswamy, Y. Liu, Separation and purification of biobutanol during bioconversion of biomass, Sep. Purif. Technol. 132 (2014) 513–540. doi:10.1016/J.SEPPUR.2014.06.013.

[18] W. Van Hecke, E. Joossen-Meyvis, H. Beckers, H. De Wever, Prospects & potential of biobutanol production integrated with organophilic pervaporation – A techno-economic assessment, Appl. Energy. 228 (2018) 437–449. doi:10.1016/J.APENERGY.2018.06.113.

[19] M. Kanemoto, H. Negishi, K. Sakaki, T. Ikegami, S. Chohnan, Y. Nitta, Y. Kurusu, H. Ohta, Efficient butanol recovery from acetone–butanol–ethanol fermentation cultures grown on sweet sorghum juice by pervaporation using silicalite-1 membrane, J. Biosci. Bioeng. 121 (2016) 697–700. doi:10.1016/j.jbiosc.2015.11.008.

[20] T. Ikegami, H. Negishi, S. Nakayama, G. Kobayashi, K. Sakaki, Pervaporative concentration of biobutanol from ABE fermentation broths by Clostridium saccharoperbutylacetonicum using silicone rubber-coated silicalite-1 membranes, Sep. Purif. Technol. 132 (2014) 206–212. doi:10.1016/J.SEPPUR.2014.05.030.

[21] S. van Wyk, A.G.J. van der Ham, S.R.A. Kersten, Pervaporative separation and intensification of downstream recovery of acetone-butanol-ethanol (ABE), Chem. Eng. Process. - Process Intensif. 130 (2018) 148–159. doi:10.1016/J.CEP.2018.06.011.

[22] A. Rom, A. Miltner, W. Wukovits, A. Friedl, Energy saving potential of hybrid membrane and distillation process in butanol purification: Experiments, modelling and simulation, Chem. Eng. Process. Process Intensif. 104 (2016) 201–211. doi:10.1016/J.CEP.2016.03.012.

[23] W. Wukovits, F. Kirchbacher, M. Miltner, A. Friedl, Assessment of Hybrid Processes for Bio-Butanol Purification Applying Process Simulation , Chem. Eng. Trans. 70 (2018) 319-324 SE-Research Articles. doi:10.3303/CET1870054.

[24] D. Korelskiy, T. Leppäjärvi, H. Zhou, M. Grahn, J. Tanskanen, J. Hedlund, High flux MFI membranes for pervaporation, J. Memb. Sci. 427 (2013) 381–389. doi:10.1016/J.MEMSCI.2012.10.016.

[25] N. Qureshi, M.. Meagher, R.. Hutkins, Recovery of butanol from model solutions and fermentation broth using a silicalite/silicone membrane, J. Memb. Sci. 158 (1999) 115–125. doi:10.1016/S0376-7388(99)00010-1.

[26] H. Zhou, Y. Su, X. Chen, Y. Wan, Separation of acetone, butanol and ethanol (ABE) from dilute aqueous solutions by silicalite-1/PDMS hybrid pervaporation membranes, Sep. Purif. Technol. 79 (2011) 375–384. doi:10.1016/J.SEPPUR.2011.03.026.

[27] K. Sakaki, H. Habe, H. Negishi, T. Ikegami, Pervaporation of aqueous dilute 1-butanol,

2-propanol, ethanol and acetone using a tubular silicalite membrane, Desalin. Water Treat. 34 (2011) 290–294. doi:10.5004/dwt.2011.2855.

[28] J.-H. Kim, D.E. Block, D.A. Mills, Simultaneous consumption of pentose and hexose sugars: an optimal microbial phenotype for efficient fermentation of lignocellulosic biomass, Appl. Microbiol. Biotechnol. 88 (2010) 1077–1085. doi:10.1007/s00253-010-2839-1.

[29] B.P. Tracy, S.W. Jones, A.G. Fast, D.C. Indurthi, E.T. Papoutsakis, Clostridia: the importance of their exceptional substrate and metabolite diversity for biofuel and biorefinery applications, Curr. Opin. Biotechnol. 23 (2012) 364–381. doi:10.1016/J.COPBIO.2011.10.008.

[30] N. Qureshi, B.C. Saha, B. Dien, R.E. Hector, M.A. Cotta, Production of butanol (a biofuel) from agricultural residues: Part I – Use of barley straw hydrolysate, Biomass and Bioenergy. 34 (2010) 559–565. doi:10.1016/J.BIOMBIOE.2009.12.024.

[31] A.M. López-Contreras, P.A.M. Claassen, H. Mooibroek, W.M. De Vos, Utilisation of saccharides in extruded domestic organic waste by Clostridium acetobutylicum ATCC 824 for production of acetone, butanol and ethanol, Appl. Microbiol. Biotechnol. 54 (2000) 162–167. doi:10.1007/s002530000374.

[32] D.T. Jones, D.R. Woods, Acetone-butanol fermentation revisited, Microbiol. Rev. 50 (1986) 484–524.

[33] D.R. Woods, The genetic engineering of microbial solvent production, Trends Biotechnol. 13 (1995) 259–264. doi:10.1016/S0167-7799(00)88960-X.

[34] L.K. Bowles, W.L. Ellefson, Effects of butanol on Clostridium acetobutylicum, Appl. Environ. Microbiol. 50 (1985) 1165–1170.

[35] K. Vollherbst-Schneck, J.A. Sands, B.S. Montenecourt, Effect of butanol on lipid composition and fluidity of Clostridium acetobutylicum ATCC 824, Appl. Environ. Microbiol. 47 (1984) 193–194.

[36] H. Azimi, H. Tezel, J. Thibault, Optimization of the in situ recovery of butanol from ABE fermentation broth via membrane pervaporation, Chem. Eng. Res. Des. 150 (2019) 49–64. doi:10.1016/J.CHERD.2019.07.012.

[37] S. Chovau, S. Gaykawad, A.J.J. Straathof, B. Van der Bruggen, Influence of fermentation by-products on the purification of ethanol from water using pervaporation, Bioresour. Technol. 102 (2011) 1669–1674. doi://doi.org/10.1016/j.biortech.2010.09.092.

[38] L.M. Vane, V. V. Namboodiri, R.G. Meier, Factors affecting alcohol-water pervaporation performance of hydrophobic zeolite-silicone rubber mixed matrix membranes, J. Memb. Sci. 364 (2010) 102–110. doi:10.1016/j.memsci.2010.08.006.

[39] T. Ikegami, H. Negishi, K. Sakaki, Selective separation of n-butanol from aqueous solutions by pervaporation using silicone rubber-coated silicalite membranes, J. Chem. Technol. Biotechnol. 86 (2011) 845–851. doi:10.1002/jctb.2598.

[40] T.C. Bowen, R.G. Meier, L.M. Vane, Stability of MFI zeolite-filled PDMS membranes during pervaporative ethanol recovery from aqueous mixtures containing acetic acid, J. Memb. Sci. 298 (2007) 117–125. doi:10.1016/j.memsci.2007.04.007.

[41] A. Faisal, M. Zhou, J. Hedlund, M. Grahn, Zeolite MFI adsorbent for recovery of butanol from ABE fermentation broths produced from an inexpensive black liquor-derived hydrolyzate, Biomass Convers. Biorefinery. (2018). doi:10.1007/s13399-018-0315-9.

[42] A. Hirsch, E. Grinsted, 543. Methods for the growth and enumeration of anaerobic spore-formers from cheese, with observations on the effect of nisin, J. Dairy Res. 21 (1954) 101–110. doi:10.1017/S0022029900007196.

[43] J. Hietaharju, J. Kangas, J. Tanskanen, Analysis of the permeation behavior of ethanol/water mixtures through a polydimethylsiloxane (PDMS) membrane in pervaporation and vapor permeation conditions, Sep. Purif. Technol. 227 (2019) 115738. doi:10.1016/J.SEPPUR.2019.115738.

[44] R. Ranjan, S. Thust, C.E. Gounaris, M. Woo, C.A. Floudas, M. von Keitz, K.J. Valentas, J. Wei, M. Tsapatsis, Adsorption of fermentation inhibitors from lignocellulosic biomass hydrolyzates for improved ethanol yield and value-added product recovery, Microporous Mesoporous Mater. 122 (2009) 143–148. doi:10.1016/J.MICROMESO.2009.02.025.

[45] M. Yang, S. Kuittinen, J. Vepsäläinen, J. Zhang, A. Pappinen, Enhanced acetone-butanol-ethanol production from lignocellulosic hydrolysates by using starchy slurry as supplement, Bioresour. Technol. 243 (2017) 126–134. doi:10.1016/j.biortech.2017.06.021.

[46] A. Oudshoorn, L.A.M. van der Wielen, A.J.J. Straathof, Adsorption equilibria of bio-based butanol solutions using zeolite, Biochem. Eng. J. 48 (2009) 99–103. doi:10.1016/J.BEJ.2009.08.014.

[47] J.Z. Yang, Q.L. Liu, H.T. Wang, Analyzing adsorption and diffusion behaviors of ethanol/water through silicalite membranes by molecular simulation, J. Memb. Sci. 291 (2007) 1–9. doi:10.1016/J.MEMSCI.2006.12.025.

[48] R. Xiong, S.I. Sandler, D.G. Vlachos, Alcohol Adsorption onto Silicalite from Aqueous Solution, J. Phys. Chem. C. 115 (2011) 18659–18669. doi:10.1021/jp205312k.

[49] W. Zhu, F. Kapteijn, J.A. Moulijn, Adsorption of light alkanes on silicalite-1: Reconciliation of experimental data and molecular simulations, Phys. Chem. Chem. Phys. 2 (2000) 1989–1995. doi:10.1039/B000444H.

[50] T. Ikegami, D. Kitamoto, H. Negishi, K. Haraya, H. Matsuda, Y. Nitanai, N. Koura, T. Sano, H. Yanagishita, Drastic improvement of bioethanol recovery using a pervaporation separation technique employing a silicone rubber-coated silicalite membrane, J. Chem. Technol. Biotechnol. 78 (2003) 1006–1010. doi:10.1002/jctb.897.

[51] M. Yu, J.L. Falconer, R.D. Noble, Adsorption of Liquid Mixtures on Silicalite-1 Zeolite: A Density-Bottle Method, Langmuir. 21 (2005) 7390–7397. doi:10.1021/la050856n.

[52] V. Saravanan, D.A. Waijers, M. Ziari, M.A. Noordermeer, Recovery of 1-butanol from aqueous solutions using zeolite ZSM-5 with a high Si/Al ratio; suitability of a column process for industrial applications, Biochem. Eng. J. 49 (2010) 33–39. doi:10.1016/J.BEJ.2009.11.008.

[53] A. Özgür Yazaydin, R.W. Thompson, Molecular simulation of water adsorption in silicalite: Effect of silanol groups and different cations, Microporous Mesoporous Mater. 123 (2009) 169–176. doi:10.1016/j.micromeso.2009.03.045.