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APPLICATION OF PERVAPORATION FOR THE IN-SITU RECOVERY OF GREEN SOLVENTS AND BIOFUELS FROM ABE FERMENTATION

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Abstract

Butanol from ABE fermentation is one well-accepted possibility of directly producing biofuels and solvents from biomass and organic residues. However, compared to butanol production from fossil resources, ABE fermentation is economically not competitive. Owing to toxicity of the products for the microorganisms, low productivity and product concentration is observed, leading to high energy demand for product recovery and purification. Thus, a highly efficient recovery process is required for productivity enhancement and product purification for final utilization. Membrane-based organophilic pervaporation among others proved to be an attractive possibility for a continuous, inline and energy-efficient solvent recovery from ABE fermentation broth. Current work focusses on the assessment of performance and separation characteristics of this process under realistic conditions. Synthetic solutions have been used to independently analyze the effects of solvent concentration and the presence of secondary components like residual sugars and nutrient salts. Two different membrane materials, POMS and PDMS, have been investigated using a lab-scale pervaporation test rig. Results indicate that an enrichment of butanol and acetone by a factor of 21 and 32 respectively, can be achieved within a single separation step.

1. Introduction

Promoted by the increase of industrialization and population the global demand for energy and material products is steadily rising. Since the primary sources for energy and chemicals are mainly based on fossil resources, this growth provokes significant issues in terms of environment, economy and society. Thus, the supply of renewable energy and sustainable chemicals became one of the major societal targets of the current century. Energy and chemicals from biogeneous resources are accepted amongst the most promising pathways for covering the growing demands both in a sustainable and economic way.

Biobutanol can be treated as a possible key substance in these regards as it acts as an energy carrier or fuel (supplement for gasoline, diesel and kerosene) and as a commodity chemical (base chemical for organic synthesis, solvent in chemical industry, raw material in fragrances and pharmaceuticals) (Dürre, 2007). It has been reported frequently that butanol outperforms ethanol as a direct fuel alternative due to its higher energy content, lower water affinity, lower vapor pressure and lower corrosively (ETIP, 2018; Qureshi et al., 2010).

While acetone-butanol - ethanol- (ABE) - fermentation as the main production route of biobutanol is a well-known technology (Gabriel,

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1928), experts agree that remarkable optimization potential is still given towards the development of an economically feasible process (Köpke et al., 2011). Significant efforts in contemporary research are undertaken towards the selection of fermentation feedstock, development and optimization of biomass-pretreatment and hydrolysis as well as metabolic engineering of the involved microorganism strains (clostridia) to enhance butanol yield and substrate utilization. A persistent challenge is the limitation of ABE fermentation by high product toxicity of butanol resulting in reasonably dilute product concentrations (up to 20 g/L) (Mariano et al., 2013). Consequently, constant in-situ separation of butanol from the fermentation broth is mandatory to sustain stable production (Bankar et al., 2012). Furthermore, butanol must be concentrated from fermentation levels up to 99.9 wt% for further utilization (downstream processing). Distillation is no option as the energy demand for butanol enrichment from typical fermenter concentration (0.5 wt%) to 99.9 wt% would exceed the thermal energy content of the product by more than 200 % (Friedl, 2016). Thus, alternative technologies for purification or pre-enrichment like gas stripping, adsorption, extraction or membrane separation have to be developed and applied (Abdehagh et al., 2014).

One highly promising method for recovering the solvents from aqueous ABE fermentation broth is membrane-based organophilic pervaporation. Pervaporation is a membrane separation process involving partial vaporization of a liquid mixture through a dense polymeric membrane. The feed is placed in contact with one side of the membrane and the permeate is removed as low-pressure vapor from the other side which is usually kept under vacuum (Lazarova et al., 2012). As a result, the separation process is not limited by the vapor liquid equilibrium as in distillation, membrane distillation or gas stripping. Moreover, fermentation temperature can be used to maintain the driving force for the separation process resulting in mild process conditions minimizing harm to microorganisms and enhancing overall economics (Rom et al., 2016).

Following an initial technical feasibility study on the applicability of PDMS and POMS membrane materials for pervaporation under ABE fermentation conditions given elsewhere (Rom et al., 2016), the focus of current work is the deeper analysis of performance characteristics of pervaporation for the extraction of products from ABE fermentation broth under realistic conditions. The influence of feed solvent concentration as well as the presence of different amounts of secondary components like residual sugars and nutrient salts will be investigated using synthetic mixtures of the involved components. For this purpose, a commercial PDMS and a more experimental POMS flat sheet membrane will be investigated. Common performance parameters will be presented which are of relevance for the selection of adequate membranes and for process development and upscaling.

2. Material and methods

2.1. Membranes

Membranes used in this work comprise two organophilic polymers of experimental and commercial type. In both cases, a number of flat sheet membranes from a single batch have been acquired and used in an existing flat sheet membrane module rack. A batch of pre-commercial POMS (polyoctylmethylsiloxane) on a PAN (polyacrylonitril) support provided by Helmholtz-Zentrum Geesthacht in Germany (batch number 16/005) has been used as the main object of analysis in current work. Commercial PDMS (polydimethylsiloxane) flat sheet membrane PERVAP™4060 has been purchased from DeltaMem AG (previously Sulzer) and was used as a reference material.

2.2. Feed solutions

N-butanol, acetone, ethanol, D-glucose and ammonium chloride of analytical grade have been used to prepare multicomponent aqueous model solutions for experimental work. Water used in this study was deionized (resistivity 18.2 MΩcm) and sanitized (TOC < 20 ppb) by Sartorius arium 611UV system. The standard feed solution comprised acetone, butanol and ethanol in a ratio of A:B:E = 3:6:1 (per weight) mixed in distilled water with an initial total solvent content of 2.5 wt%.

During experimental analysis, this initial content has been lowered due to depletion by pervaporation as well as by dilution with additional water. This allowed for the analysis of a broader range of total feed solvent content (around 1.0 wt% up to 2.5 wt%) corresponding with the expected contents in real ABE fermentation broths.

For investigation of the influence of fermentation broth secondary components, this solution was complemented by addition of D-glucose and ammonium chloride in certain amounts up to an extent of 200 and 3.0 g/L, respectively, representing not consumed sugars and present nutrient salts. NH_4Cl has been chosen as a representative for a broader variety of nutrition salts like K_2HPO_4, KH_2PO_4, $MgSO_4$, $FeSO_4$ and $MnSO_4$ usually used in ABE fermentations. Typical fermentation media contain around 2.0 g/L of NH_4Cl, around 0.25 g/L of each potassium salt and lesser amounts of trace nutrient salts. Thus, an amount of 3.0 g/L of NH_4Cl chosen as a summed-up representative seems reasonable.

While a significant increase of permeance and separation factor has been reported for increasing feed temperature (Rom et al., 2016), it has been decided to only consider pervaporative product recovery at fermentation temperature in current work for obvious energy efficiency reasons. Thus, 35°C and 10 mbar(a) have been kept constant for feed temperature and permeate pressure, respectively.

2.3. Pervaporation experimental setup

Pervaporation experiments have been conducted using a laboratory pervaporation setup depicted in Fig. 1. 2500 ml of the feed are provided in the feed tank (1) which is placed on a scale for permanent monitoring (2). The feed solution is recirculated using a feed pump (3) at a constant flow rate of 100 l/h and is heated up to a constant temperature of 35°C with a thermostatized heat exchanger (4). Two membrane module racks are provided in this setup, a hollow fiber rack (5) and a flat sheet membrane module rack (6), only the latter to be used in current work. The flat sheet membrane module is made of a stainless steel corpus with an inner lining of Teflon and offers an active membrane surface area of 144 cm². The relatively small surface area together with the large volume flow ratio for the feed results in a negligible stage-cut and negligible differences in feed and retentive compositions and thus allowing for simple calculator analysis of the experimental results. The permeate is collected under vacuum of 10 mbar(a) provided by an oil sealed rotary vane vacuum pump (8) and captured in cold traps (7) cooled with liquid nitrogen to ensure total condensation at low pressures.

As experiments with non-volatile glucose and salt have been conducted, repetitive experiments with water and ABE standard solution have been performed in order to identify potential permanent flux decline due to fouling and scaling on the membrane surface.

Experimental operation was maintained under constant conditions for 1 hour after which the collected permeate was thawed and sampled for analysis while the depletion of solvents in the feed solution was monitored repeatedly by sampling for analysis. Especially permeate samples had to be diluted before sampling as phase separation occurred frequently depending on the actual butanol enrichment factor.

2.4. Analytical procedure and determination of performance indicators

Analysis of the composition of feed and permeate samples has been conducted using the gas chromatography system GC-2010 Plus with FID detector from Shimadzu Corporation and an AOC-5000 autoinjector system. The GC was equipped with an Elite-WAX ETR capillary column from PerkinElmer Inc. (length: 30 m, inner diameter 0.32 mm). The temperature program started with an initial temperature of 30 °C for 6 min, then raised it to 200 °C with a ramp of 20 °C/min and was maintained at this temperature for 1 min. Split was set to 20 with an injection volume of 1 µl (Rom et al., 2016).

Pervaporation transmembrane flux can be described using the solution-diffusion model introduced by Wijmans and Baker (Wijmans et al., 1995). Thus, the driving force of the process is the partial pressure difference between the liquid feed side and the vapor permeate side. The proportionality factor combining the driving force for component i in the feed mixture and area-specific transmembrane component flux is called permeance (Eq. 1).

Partial pressure on the liquid feed side is calculated using molar fraction of component i derived from GC analysis, saturation pressure of component i at feed temperature (calculated using Antoine correlation and parameters taken from NIST, 2018) and activity coefficient of component i at infinite dilution in water (determined by Aspen Properties V10 using NRTL method, binary interaction parameters for water, ethanol and acetone taken from APV100 VLE-IG database, binary interaction parameters of butanol in water taken from Rom et al., 2014). Partial pressure on the gaseous permeate side is calculated using molar fraction of component i derived from GC analysis and the set total permeate pressure of 10 mbar(a). If transmembrane component fluxes are experimentally accessible, presences for each component can be derived by simple rearrangement (Eq. 2).

$$J_i = \pi_i (\gamma_i p_i^{sat} x_i - p_{perm_{y_i}})$$ (1)

$$\pi_i = \frac{J_i}{(\gamma_i p_i^{sat} x_i - p_{perm_{y_i}})}$$ (2)

Using the current experimental setup, area-specific transmembrane flux of component i is calculated from total collected permeate mass, content of component i in the permeate, membrane area and the duration of an experiment of 1 hour (Eq. 3).

$$J_l = \frac{m_i}{A_t}$$ (3)

Three different selectivity measures for characterizing pervaporation performance are commonly used. The enrichment factor is given by the weight fraction of a component i in the concentrate divided by the weight fraction of this component in the feed solution. In case solvents are considered, permeate represents the concentrate stream (Eq. 4).

The separation selectivity of the membrane for component i over component j can be calculated as a ratio of the permeance and is usually referred as permselectivity (Eq. 5). To characterize the process as a whole, the separation factor is recommended being calculated from the weight fractions of components i and j in the feed f and permeate p streams (Eq. 6).

$$\varepsilon_l = \frac{w_{pi}}{w_{fi}}$$ (4)

$$\alpha_{ij} = \frac{\pi_i}{\pi_i}$$ (5)

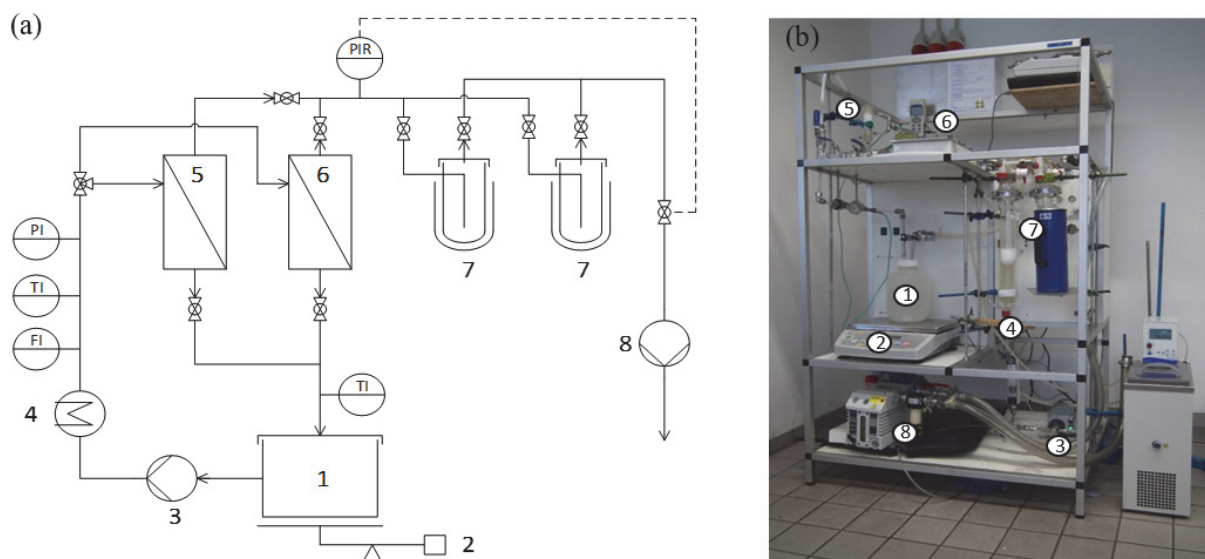$$\beta_{ij} = \frac{w_{fi} w_{pj}}{\pi_i w_{pi}}$$ (6)

Fig. 1. Scheme (a) and photograph (b) of the used laboratory pervaporation setup

Perm selectivity and separation factor as selectivity/quality measures are complemented by permeance (Eq. 2) or pervaporation separation index PSI (Eq. 7) for quantitative characterization of the membrane performance. These measures are commonly used as performance indicators for pervaporation processes and for the comparison of different membrane materials.

$$PSI_I = (\beta_{ij} - 1)\Sigma_{i=1}^{n} J_i \qquad (7)$$

3. Results and discussion

The influence of certain fermentation broth secondary components on the characteristics of pervaporation product recovery has been analyzed in current study with a special focus on residual sugars and nutrient salts. Consequently, the influence of D-glucose and of ammonium chloride as relevant representatives on the apparent transmembrane flux has been investigated and is presented in the following.

Concerning potential permanent transmembrane flux decline, analysis of repeated experiments using pure water and pure aqueous ABE mixtures it can be summarized that scaling and fouling has not been occurring for both analyzed membranes and all applied operational conditions.

3.1. Glucose dependence

First step in the analysis of influences on pervaporation performance is the quantification of component fluxes at different conditions as a quantitative measure. In current work, the components butanol, acetone, ethanol and water are considered. Transmembrane component fluxes of butanol and acetone as a function of solvent and glucose contents in the feed are given for both analyzed membranes in Fig. 2. Despite the substantial spreading of results for

the commercial PDMS membrane arising from the reduced number of experimental repetitions, a linear correlation of solvent flux and solvent content in the feed is apparent within the analyzed range of feed concentration. This is a direct result and verification of applicability of the solution-diffusion model indicating a linear influence of the driving force on the component flux (Eq. 1). The linear fit with a very high correlation coefficient further indicates that the permeate partial pressure term in Eq. (1) is almost negligible due to the very low permeate total pressure and that the driving force, as a first approximation, is a function of feed concentration only. While not shown explicitly here, the same behavior was also monitored for the component ethanol. For water on the other hand, this linear correlation has not been observed. The transmembrane water flux was constant over the whole analyzed range of feed water content due to the fact that the relative change in water content was negligible compared to the absolute water content (ranging between 97.5 and 99.0 wt%).

Considering experimental results with different glucose contents in the feed, it becomes obvious that no influence on the transmembrane component fluxes can be determined for glucose contents of up to 50 g/L in the feed. Only at a very high content of 200g/L glucose in the feed, a small reduction of the transmembrane fluxes has been monitored compared to the fluxes without any glucose: butanol -15 %, acetone - 23 %, ethanol - 17 %, and water - 16 %. Repeated experiments with pure water and ABE-water mixtures indicate, that this reduction is not a permanent flux decline e.g. due to scaling or fouling, but is a reversible effect solely arising at high glucose contents. It is assumed that this flux reduction for all permeating components is a result of concentration polarization of the non-permeating component glucose.

Comparing POMS results with results of commercial PDMS membrane, it has to be mentioned,

that fluxes are considerably higher for PDMS membrane. Thus, it is expected that the required membrane area for a given feed volume flow rate is lower for the commercial PDMS than for the more experimental POMS membrane material.

To derive a measure for the glucose influence on the pervaporation performance in terms of quality, the enrichment of solvents from feed to permeate is the easiest possibility.

Fig. **3** shows the concentration of butanol in the permeate as a function of butanol and glucose concentration in the feed. Again, a linear correlation can be found suggesting that the enrichment factor of solvent is independent of solvent content in the feed,

at least in the analyzed range. This statement also holds true for acetone and ethanol and is found for both membrane materials again confirming the applicability of Eq. 1 with constant permeance. No difference in the results can be observed between all analyzed glucose feed contents, not even at the highest content. While the quantitative measure of transmembrane fluxes is declining at high glucose contents, the qualitative measure of solvent enrichment (and also perm selectivity and separation factor) stays constant since all components are influenced by the flux decline at high glucose contents to a very similar extent. Comparing the two different membrane materials, no significant difference can be found in the separation quality.
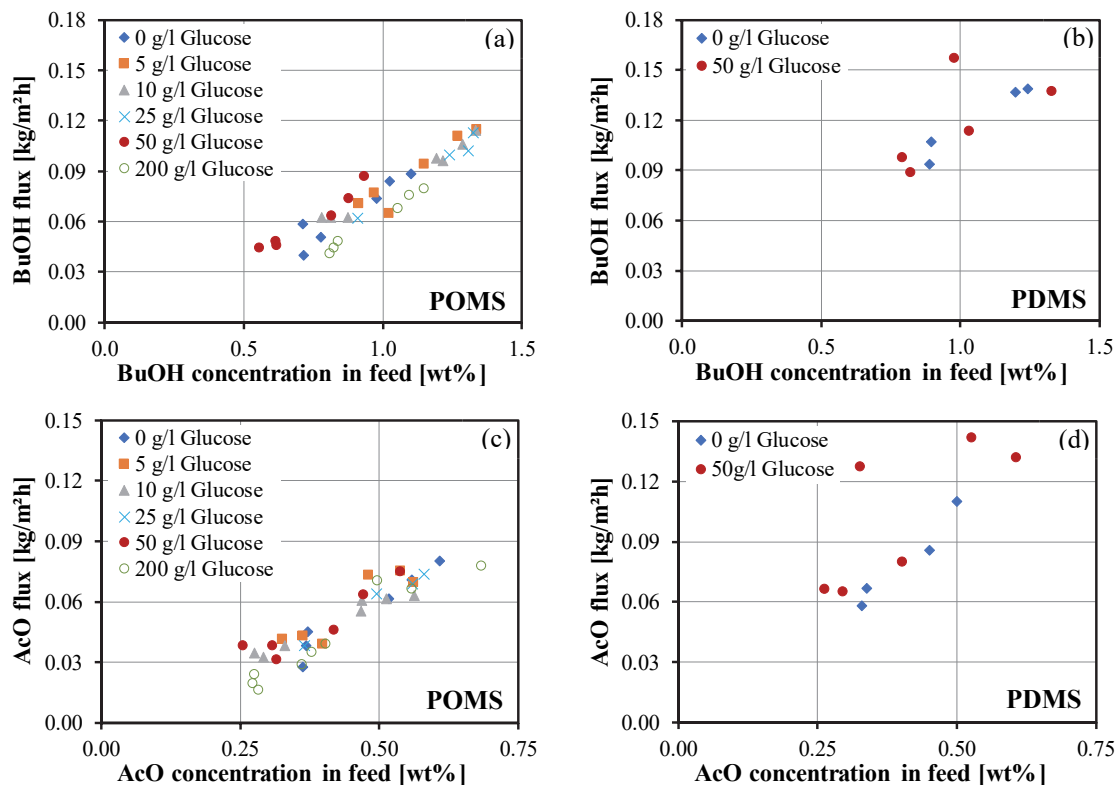

Fig. 2. Transmembrane butanol (a, b) and acetone (c, d) fluxes as a function of solvent and glucose concentration in synthetic ABE feed solution for POMS (a, c) and PDMS (b, d) membranes
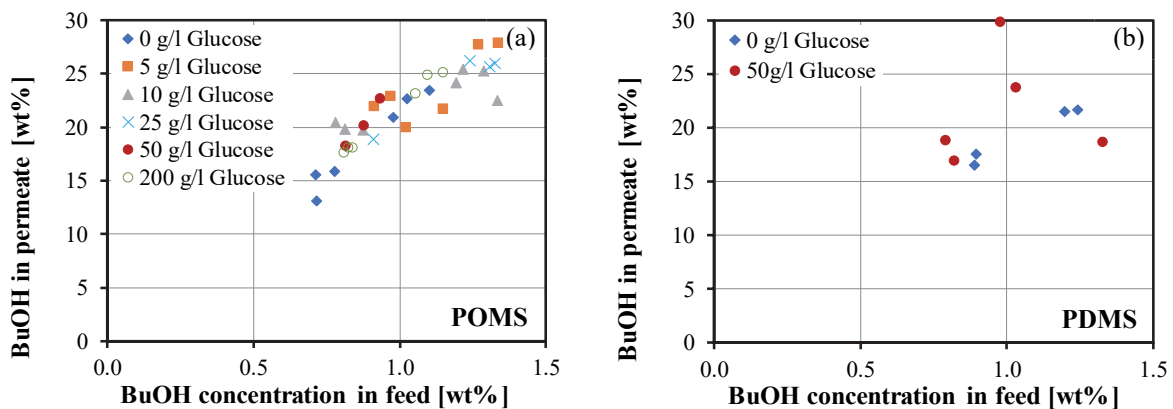

Fig. 3. Butanol concentration in permeate as a function of butanol and glucose concentration in synthetic ABE feed solution for POMS (a) and PDMS (b) membranes

To sum up, very high amounts of glucose lead only to a reduction of the flux while the quality of the separation stays constant. For glucose contents relevant for real ABE fermentation broths after solventogenesis (maximum of 50 g/L), no influence on pervaporation performance is expected at all (quantity and quality).

3.2. Salt dependence

A similar approach to the one presented for glucose has also been applied for analyzing the influence of salt on the pervaporation characteristics revealing similar behavior. Fig. 4 shows the transmembrane component fluxes of butanol and acetone as a function of solvent and salt contents in the feed for both analyzed membranes. The same linear trend is observable like for glucose and no influence of the content of ammonium chloride is detectable. Ethanol exhibits the same behavior as butanol and acetone while transmembrane water fluxes are constant for all salt concentrations. It is concluded that the presence of salt in the analyzed concentration range does not change the activity of the remaining components and thus does not influence the

pervaporation driving forces and the transmembrane fluxes. As for glucose, PDMS membrane gives clearly higher transmembrane fluxes than POMS membrane. A higher flux and a distinctively higher slope become obvious especially for acetone for the PDMS membrane indicating a clearly higher permeance in this case. This will be pointed out in detail in section 3.3.

The enrichment of butanol depending on the contents of butanol and ammonium chloride in the feed for both membrane materials is given in Fig. 5 showing the butanol content in the permeate. As all component fluxes are not influenced by the presence of salt, it is unsurprising that also the quality of the separation (enrichment, permselectivity and separation factor) is not changed in the examined concentration range. While the fluxes are higher for the PDMS membrane, Fig. 5 reveals that POMS reaches slightly higher permeate butanol concentrations and therefore a higher enrichment factor resulting in a qualitatively improved separation, at least for butanol. Compared to that, analysis shows quite similar results for acetone and ethanol for both membranes especially when considering measurement uncertainties.
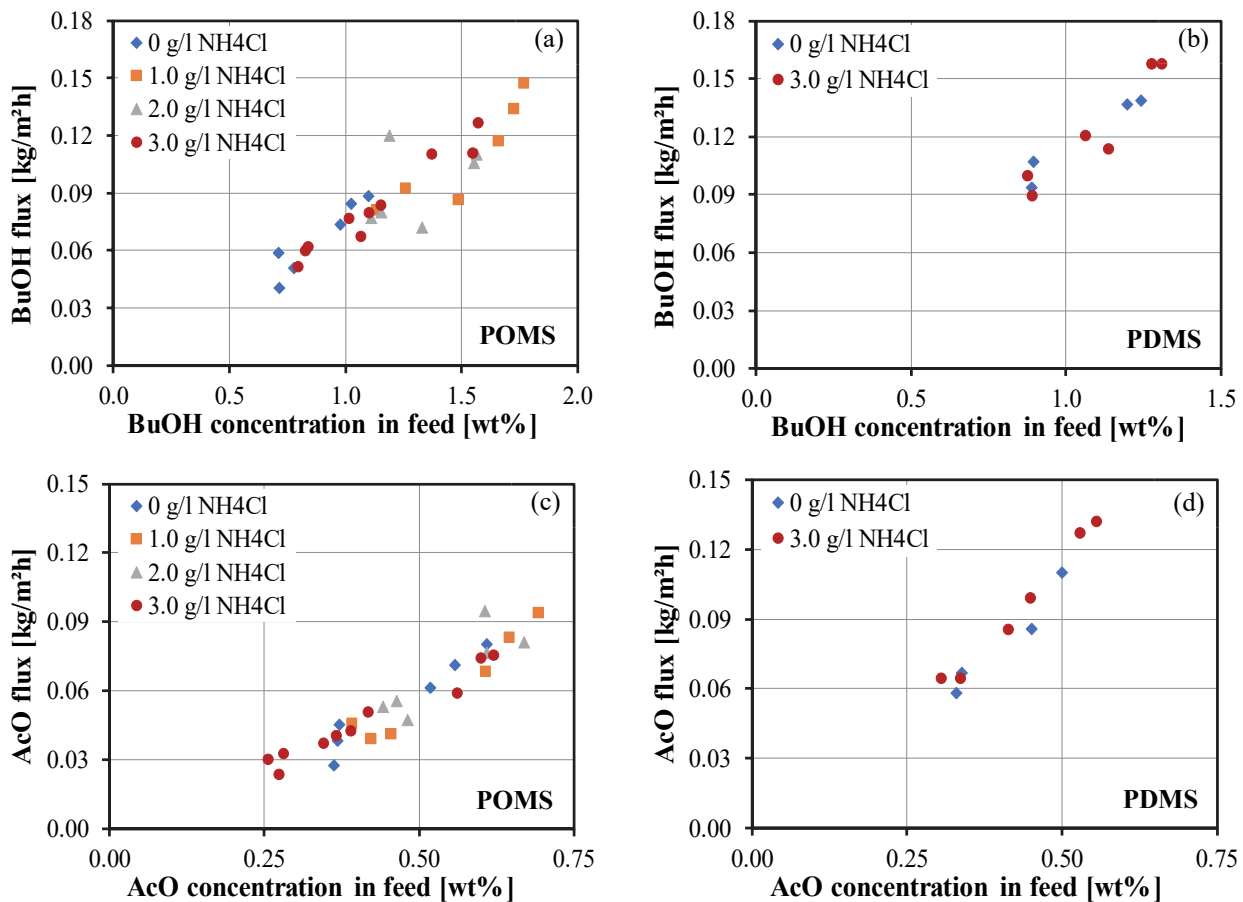

Fig. 4. Transmembrane butanol (a, b) and acetone (c, d) fluxes as a function of solvent and salt concentration in synthetic ABE feed solution for POMS (a, c) and PDMS (b, d) membranes
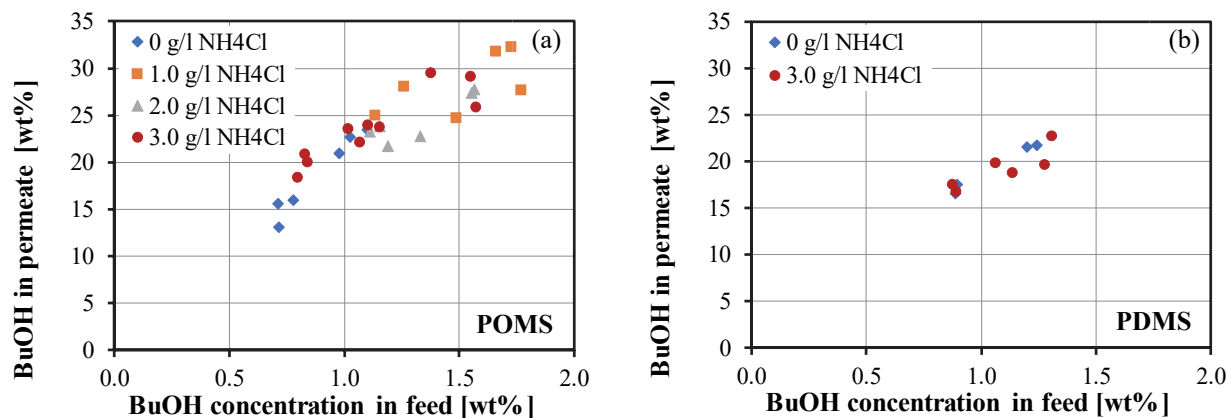
Fig. 5. Butanol concentration in permeate as a function of butanol and salt concentration
in synthetic ABE feed solution for POMS (a) and PDMS (b) membranes

3.3. Cumulative pervaporation performance parameters

While former sections were dedicated to revealing the influence of concentrations of solvents, glucose and salt on the pervaporation characteristics, differences of the analyzed membrane materials will be pointed out in the following. In order to do so, experimental results with different solvent contents, salt contents and glucose contents (except the ones for 200 g/L) are combined and common performance indicators are calculated according to equations in section 2.4. Results from experiments with 200 g/L of glucose content in the feed have been omitted from this assessment as pervaporation under this condition resulted in slightly lower transmembrane fluxes as described in section 3.1.

Both qualitative measures (permselectivity, separation factor) and quantitative measures (permeance) are of relevance and presented. Moreover, the widely accepted combined parameter PSI is given. As this parameter incorporates a certain fixed weighting between quality and quantity it must be treated with care and should only be taken as a rough guiding value. Results for both membrane materials are presented in Table 1. All values are given with standard deviation as an uncertainty measure of the experimental procedure. In order to compare data from current work with published literature values, a recent publication of Van Hecke and co-workers has been chosen (Van Hecke and De Wever, 2017). In this work, authors determined the performance of commercial POMS and PDMS membranes (PERVATECH, The Netherlands) during the pervaporation of real ABE fermentation broths using artificial as well as real lignocellulosic hydrolysates as substrates. Solvent and water transmembrane fluxes from this work have been used to calculate permeances comparable to values in current work. In addition, PSI values and separation factors are taken from Van Hecke and De Wever, 2017 as they have been determined using similar feed compositions

resulting in a direct comparability. Values derived are in good accordance with own experimental results applying POMS and PDMS membranes from PERVATECH (Adorjan, 2019). Nevertheless, converted results from Van Hecke and De Wever, 2017 are partly connected to considerable uncertainty (5 to 15 %) because permeate pressures relevant for the calculations are only given as a range and not as precise values.

Relatively low permselectivity values indicate that most of the separation effect in ABE pervaporation emanates from different activities and vapor pressures of solvents and water, whereas the selectivity of the membrane only plays a minor role. Values for both membrane materials are relatively similar. While permselectivity for acetone and ethanol seems to be slightly lower for POMS, the value is higher for butanol. This becomes more obvious for the separation factor of butanol/water, which is increased for POMS even under consideration of measurement uncertainties. For acetone/water and ethanol/water no significant difference has been monitored. Separation factors for acetone and butanol are high enough to anticipate an attractive separation process performance with enrichment factors from feed to concentrate (permeate) in the range of 32 and 21, respectively. Enrichment factors for ethanol are around 6 for both membranes and at this order of magnitude of no interest for further exploitation. Nevertheless, ethanol can be regarded as a side product in ABE fermentation (refer to the typical ABE ratio in fermentation broths of 3:6:1 per weight), which is produced only in very limited amounts and concentrations. Consequently, the poor selectivity for ethanol is only a marginal drawback for applying pervaporation in ABE recovery using the considered membrane materials.

Proceeding to the quantitative measure, the development status of the commercial membrane becomes apparent. PDMS membrane exhibits almost double permeance for acetone and ethanol and still +50 % for butanol.

Table 1. Pervaporation performance parameters for two different flat sheet membranes at 35°C feed temperature
and 10 mbar (a) permeate pressure compared to parameters derived from literature values (Van Hecke and De Wever, 2017)

	Current work		*Van Hecke and De Wever, 2017*	
	POMS (HZG)	*PDMS (DeltaMem)*	*POMS (PERVATECH)*	*PDMS (PERVATECH)*
Permselectivity [-]				
Acetone/water	0.99 (±0.21)	1.18 (±0.65)	0.34 (±15 %)	0.34 (±5 %)
Butanol/water	2.45 (±0.50)	2.35 (±1.14)	1.49 (±15 %)	1.07 (±5 %)
Ethanol/water	0.79 (±0.15)	0.90 (±0.31)	0.57 (±15 %)	0.84 (±5 %)
Separation factor [-]				
Acetone/water	51.2 (±9.3)	53.3 (±8.5)	26.8	21.6
Butanol/water	33.0 (±5.6)	29.0 (±4.3)	19.5	18.8
Ethanol/water	9.0 (±1.4)	9.2 (±1.1)	8.0	8.9
Permeance [mol/m²hbar]				
Acetone	264 (±52)	500 (±148)	618 (±15 %)	206 (±5 %)
Butanol	665 (±191)	1002 (±268)	2707 (±15 %)	654 (±5 %)
Ethanol	211 (±32)	388 (±69)	1043 (±15 %)	513 (±5 %)
Water	273 (±59)	450 (±72)	1818 (±15 %)	609 (±5 %)
PSI [mol/m²h]				
Acetone/water	760 (±51)	1301 (±8)	121-911	81-303
Butanol/water	484 (±29)	696 (±3)	66-302	57-227
Ethanol/water	121 (±3)	204 (±0.1)	63-302	30-234

It is assumed that a thicker selective membrane layer or a thicker coating layer causes these low permeances for the POMS membrane but this assumption is uncertain, as values for both membranes have not been communicated. However, the also lower water permeance for the POMS membrane finally leads to relatively similar permselectivities for the two membranes. It is a question of the development potential of the experimental material whether permeances can be increased without hampering selectivity. At this point, analysis of PSI gives the same conclusions as an analysis of permeance values.

Comparing results from current work with data from literature is difficult, as Van Hecke and De Wever, 2017 used real fermentation broth for examination and membranes from a different vendor. It is obvious that separation factors for real fermentation broths are significantly lower than for synthetic mixtures, which has already been communicated in literature quite frequently. PSI values are comparable for both membrane materials but permeances and permselectivities show a very pronounced hydrophilic behavior for the membranes reported in Van Hecke and De Wever, 2017. While this can partly also be attributed to the utilization of real fermentation broth, a more detailed analysis is necessary in order to facilitate deeper understanding of this behavior.

4. Conclusions

Based on preceding work (Rom et al., 2016) current contribution presents a structured analysis of the application of membrane-based pervaporation for the extraction of acetone, butanol and ethanol from ABE fermentation broth. The influence of secondary components to be expected in ABE fermentation broth after solventogenesis on pervaporation performance has been determined regarding contents of residual sugar and nutrition salts. For this purpose, synthetic mixtures of acetone, butanol, ethanol and water have been complemented with different amounts of D-glucose and ammonium chloride. Pervaporation experiments have been conducted using an existing lab-scale experimental setup. Two different membrane materials have been investigated at constant temperature of 35°C and constant permeate pressure of 10 mbar(a): one pre-commercial POMS flat sheet membrane from Helmholtz Zentrum Geesthacht and a commercial PDMS flat sheet membrane from DeltaMem AG.

Results indicate that ammonium chloride has no influence on transmembrane fluxes and solvent enrichment within the analyzed concentration range of 0 to 3.0 g/L of salt. Also for glucose content in the feed solution no influence has been monitored for levels relevant for real ABE fermentation broths after solventogenesis (50 g/L). Only at very high glucose contents (200 g/L) a decline of transmembrane fluxes of all monitored components has been detected (15-23%). As this flux decline is very similar for solvents and water, no decrease of selectivity has been observed.

Referring to the comparison of the two membrane materials in terms of common performance indicators, it has been shown that the separation selectivity of POMS and PDMS are basically identical when considering the uncertainties of the applied methods with a small superiority for POMS in butanol separation factor. Nevertheless, considering the absolute flux, the commercial PDMS membrane outperforms the pre-commercial POMS membrane by 50 to almost 100 %. Comparing membranes used in current work with different membranes from literature reveals remarkable differences between individual membrane vendors and different membrane behavior when real fermentate is used instead of synthetic mixtures.

With an enrichment of solvents from dilute aqueous solutions by a factor of 20 to 30 in a single

separation step, organophilic pervaporation proves to be an efficient and economic recovery method for products from ABE fermentation. It is a simple and robust process suitable to significantly decrease the energy demand for recovery and dehydration compared to a multi-staged distillation approach.

It has been shown that secondary components glucose and salts do not influence the separation process in a negative way. In the next steps, the assessment on secondary components will be extended to organic acids as intermediate products during the two-staged ABE fermentation (acidogenesis/solventogenesis). For this purpose, the influence of acetic acid and propionic acid will be analyzed in a structured way. Propionic acid will be used as a representative for the precursor butyric acid as it is far easier to handle in the lab and the behavior during pervaporation is almost identical.

Finally, the survey will be expanded to other commercial and non-commercial membrane materials as well as different membrane module layouts. This expanded survey will especially include the membranes which have been reported in Van Hecke documents and will also contain an analysis of the difference between real and synthetic fermentation broths.

Nomenclature

A	membrane area	m²
α_{ij}	permselectivity of component i over component j	-
β_{ij}	separation factor of component i over component j	-
γ_i	activity coefficient of component i	-
ε_i	enrichment factor of component i	-
J_i	transmembrane flux of component i	kg/m²h
m_i	mass of component i in collected permeate	kg
p_i^{sat}	saturation pressure of component i	bar
Π_i	permeance of component i	kg/m²hbar, mol/m²hbar
p_{perm}	total pressure on permeate side	bar
t	duration of experiment	h
w_{fi}	weight fraction of component i in feed	-
w_{pi}	weight fraction of component i in permeate	-
x_i	molar fraction of component i on feed side	-
y_i	molar fraction of component i on permeate side	-

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