



Effect of butanol, ethanol and acetone feed composition through activated carbon-containing polydimethylsiloxane pervaporation membrane

Efeito da composição de alimentação de butanol, etanol e acetona na pervaporação através de membranas de polidimetilsiloxano contendo carvão ativado

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The ABE route, whose products are acetone, butanol and ethanol, is an industrial process that has been investigated by the possibility of incorporating renewable resources as inputs of chemical compounds and fuels. In view of the toxicity of 1-butanol to the cells of the fermentation broth, pervaporation by means of a polydimethylsiloxane mixed matrix membrane containing 1 wt% activated carbon was used as an alternative to recover this alcohol simultaneously to its production. Synthetic aqueous solution of acetone, 1-butanol and ethanol was investigated with total organic content varied from 1.5 to 2.7 wt%. Permeate flux and selectivity (separation and enrichment factors) were reported. Regarding the organics transport through the membrane, there was not a linear relation of their content in feed stream and flux. Besides, the permeation sequence did not follow a single transport mechanism. High separation and enrichment factors for acetone and butanol were observed.

Keywords: biofuel, mixed matrix membrane, separation.

A rota ABE, cujos produtos são acetona, butanol e etanol, é um processo industrial que tem sido investigado pela possibilidade de incorporação de fontes renováveis como matéria-prima para produtos químicos e combustíveis. Considerando a toxicidade do 1-butanol para as células do mosto fermentativo, a pervaporação através de membrana de matriz mista de polidimetilsiloxano contendo 1% em massa de carvão ativado foi usada como alternativa para recuperar este álcool simultaneamente à sua produção. Soluções aquosas sintéticas de acetona, 1-butanol e etanol foram investigadas com teor total variando de 1,5 a 2,7% em massa de orgânicos. O fluxo e a seletividade do permeado (fatores de separação e de enriquecimento) foram medidos. Em relação ao transporte de orgânicos pela membrana, não houve relação linear entre a concentração na alimentação e o fluxo. Além disso, a sequência de permeação não seguiu um único mecanismo de transporte. Foram observados elevados fatores de separação e enriquecimento para acetona e butanol.

Palavras-chave: biocombustível, membrana de matriz mista, separação.

1. INTRODUCTION

ABE fermentation is a known process for butanol production by means of *Clostridium acetobutylicum*. It results in acetone (A), 1-butanol (B) and ethanol (E) and it has been investigated to replace the oxo process for butanol synthesis using biomass. On the other hand, oxo process is based on a catalytic reaction between propylene, CO and H₂, leading to n-butyraldehyde and isobutyraldehyde, which is hydrogenated to produce iso and n-butyl alcohols. Afterwards, these alcohols are separated by distillation [1]. The possibility of incorporating renewable resources instead of petroleum derivatives in the energy and chemical industries is highly demanded by the society. However, the ABE process has low yield due to the toxicity of 1-butanol to the cells in concentrations above 20 g/L [2], making mandatory its removal from the broth.

Pervaporation using mixed matrix membrane of polydimethylsiloxane (PDMS) with activated carbon has been studied aiming at high permeate flux associated with high separation factor of 1-butanol from fermentative broth. This condition can ensure greater efficiency in 1-butanol

recovery allowing the substitution of oxo route. However, according to the literature, this process has not been successful yet, since the permeate flow is favored over the separation factor. The improve in membrane characteristics is still a barrier to be overcome [3].

Azimi and co-workers analyzed the influence of activated carbon (AC) in PDMS in face of butanol-water binary solution. They reported a separation factor of 25.2 and permeate flux of $44.5 \text{ kg/m}^2\text{s}$ [3]. Li and co-authors worked with a triple composite membrane (PDMS/PE/Brass) which is formed by an active layer of PDMS, a support layer of high porosity polyethylene (PE) and a support layer of perforated metal (Brass) of high mechanical strength [4]. They analyzed the interaction of PDMS/PE/Brass under different membrane thicknesses in 1-butanol solution and observed the inverse relationship between the separation factor and the permeate flux.

The goal of this work was the investigation of the permeation flux through a 1 wt% AC dispersed in PDMS, varying the organic content (ABE content) in aqueous solution, in a synthetic solution to mimic fermentation broth. Feed was composed of quaternary solutions of 1-butanol, acetone, ethanol and water with organic content ranging from 1.5 to 3.0 wt%. The membrane selected here was prepared and characterized in a previous work [5] and showed the highest free fraction volume.

2. MATERIALS AND METHODS

2.1 Materials

Activated carbon (Merck) with a mean particle diameter of $23.4 \mu\text{m}$ and a surface area of $855 \text{ m}^2/\text{g}$, Polystic silicon glue (Pulvitec), toluene (Nuclear, 99.8%), acetone (Synth, 100%), 1-butanol (Synth, 99.8%), and ethanol (Synth, 99.5%) were used.

2.2 Membrane preparation

Polystic glue and toluene were added to a plastic flask which was magnetically stirred for 40 min at $25 \text{ }^\circ\text{C}$. Activated carbon was added so that the content was 1 wt% relative to the polymer used. The system was transferred to a Teflon plate, placed in a fume hood for 24 hours at $25 \text{ }^\circ\text{C}$, followed for an oven at $120 \text{ }^\circ\text{C}$ for 1 hour. The membrane was characterized with respect to thickness, scanning electron microscopy, SEM, Fourier transform infrared spectroscopy, FTIR, thermogravimetric analysis, TGA, and positron annihilation spectroscopy, PALS, as described in the literature [5].

2.3 Pervaporation tests

Pervaporation tests were performed by pumping (Masterflex, Millipore) the quaternary solution from the feed tank to the membrane cell so that the permeate was recovered in a U-shaped tube immersed in liquid nitrogen. The experimental setup is shown in Figure 1. The permeate stream was kept under vacuum (Edwards, E2M0.7). After 4 and 8 hours of the experiment, the permeate was removed from the tube and analyzed. Feed solutions were prepared with 1-butanol concentration in the range of 6 to 24 g/L (0.85 to 1.6 wt%). Butanol/acetone/ethanol weight relation was kept in 6:3:1, as in the typical fermentation broth. These conditions led to an organic content ranging from 1.5 to 2.7 wt%. The temperature of the tests was set at $25 \text{ }^\circ\text{C}$ and the ratio of membrane area (63 cm^2) to feed solution volume 15.62 m^{-1} .

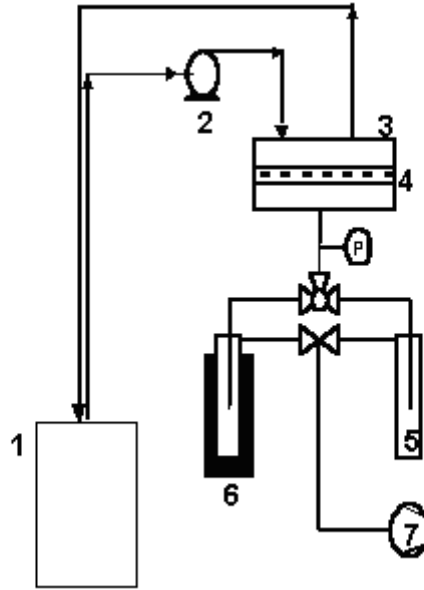


Figure 1: Experimental pervaporation setup. 1- Feed tank, 2 – drive pump, 3 – pervaporation cell, 4 – membrane, 5 – condenser, 6 – liquid nitrogen, 7 – vacuum pump. Source: Gonçalves et al. (2019) [5].

Flux and selectivity (alpha and beta) were calculated by means of Equations 1, 2 and 3. In Equation 1, j is the mass flux, in $\text{g}/\text{m}^2\text{h}$, m is the permeate mass, in gram, A is membrane area, in square meters and t is the experiment time, in hour. In Equations 2 and 3, alpha and beta are the separation and enrichment factors, w_i and w_w are the mass fraction of the organic i (butanol, ethanol or acetone), and water, while subscript perm and feed refers to permeate or feed stream [6].

$$j = \frac{m}{A \cdot t} \quad (1)$$

$$\alpha = \frac{(w_i/w_w)_{\text{Perm}}}{(w_i/w_w)_{\text{Feed}}} \quad (2)$$

$$\beta = \frac{(w_i)_{\text{Perm}}}{(w_i)_{\text{Feed}}} \quad (3)$$

Pervaporation tests were performed in duplicates, since flux and selectivity results showed deviations lower than 5% and the results were reported as the average of the runs. Butanol, acetone and ethanol were determined in triplicates by gas chromatography (Shimadzu, CG17A), through column Carbowax 20M as described elsewhere [5]. Water content in feed solutions was determined by a mass balance, while in permeate it was determined by Karl Fischer method (Titronic 300) [5].

2.4 Membrane Permeability Calculation

Membrane permeability, P_i , in mol/mhPa , was calculated by using Equation 4, in which J is the molar flux of the specie ($\text{mol}/\text{m}^2\text{h}$), l is membrane thickness (m), x_i is the molar fraction of the specie in feed stream, γ_i is the activity coefficient, equal to 1 due to the dilute aqueous solution, p_i^0 is the saturation pressure (Pa), y_i is the molar fraction of the specie in the permeate stream and p_p is the partial pressure of the specie in the permeate, equal to zero due to the low pressure in this stream. Equation 5 shows the assumptions of γ_i and p_p equal to zero in Equation 4.

$$P_i = \frac{J_i * l}{(x_i \gamma_i p_i^0 - y_i p_p)} \quad (4)$$

$$P_i = \frac{J_i * l}{x_i p_i^0} \quad (5)$$

3. RESULTS AND DISCUSSION

3.1 Membrane characterization

Membrane characterization was performed in another paper [5]. Briefly, membrane thickness was 220 μm . SEM results showed that the membrane with AC 1 wt% showed similar morphology to pure PDMS films. TGA and FTIR results did not change significantly due to the low content of the filler, however, PALS results showed an increase in both the free fraction volume and concentration of the voids compared to pure PDMS in 6.5% and 8.8 %, respectively.

3.2 Pervaporation tests

The choice of the AC-containing PDMS membrane with 1 wt% of the filler was based in previous results [5]. Although the membrane has shown the highest thickness (220 μm) of the skin layer, the highest free volume, flux and selectivity of butanol against water at 55 $^{\circ}\text{C}$, motivated this study upon varying butanol content in the feed stream.

The results of pervaporation tests are presented in Table 1. Values are the average of two runs. It was not possible to detect ethanol in permeate in any experimental condition. The low content of ethanol in feed is one of the reasons for this behavior, since the driven force for transportation is very tiny. It could also be ascribed to the low sensibility of the gas chromatography to this chemical. Another hypothesis is that ethanol is the lowest carbon chain, which could make its permeation harder, specially combined to the highest polarity compared to butanol and acetone.

Table 1: Experimental results of the pervaporation tests.

Feed content (wt%)				Permeate content (wt%)				Total flux (g/m ² h)	α		β	
Acetone	Butanol	Ethanol	Water	Acetone	Butanol	Ethanol	Water		Acetone	Butanol	Acetone	Butanol
0.50	0.85	0.15	98.5	39.82	44.41	-	15.77	12	521	368	78	55
0.58	1.15	0.29	97.99	29.32	61.66	-	9.02	16	547	540	53	52
0.81	1.63	0.27	97.28	32.79	57.55	-	9.66	14	451	402	40	36

Regarding the permeate flux, it was noted that it was lower than the ones reported for similar systems in the literature [7-9]. This low value is related to the skin thickness of such membrane (220 μm). The total flux did not increase linearly with the organic content in feed stream, indicating that the increase in organic content is not the main drive force for permeation, as expected. The highest value of flux was observed for the total organic content of 2 wt% (intermediate condition). Besides, the flux sequence was $J_{\text{butanol}} > J_{\text{acetone}} > J_{\text{water}} > J_{\text{ethanol}}$, which is neither related to the saturation pressure of the components, nor their kinetic diameter or affinity to PDMS [10, 11]. This unusual behavior is due to more than one driven force for the transport, probably the adsorption of the chemicals (acetone and butanol) combined with the saturation pressure and affinity of them to the PDMS matrix. In previous work, the higher content of

activated carbon caused an increase in butanol flux. Also, the increase in test temperature increased its permeation, probably favoring the desorption [5]. However, it seems that the saturation pressure caused the permeation of butanol, which might be combined to the adsorption sites. Regarding acetone, the transport could have been facilitated both to the affinity to PDMS and adsorption in activated carbon. Ethanol did not permeate due to its low content in feed stream together with the low affinity to the polymer and the filler. Water permeation can be due to the huge concentration in feed together with its small size (kinetic diameter).

Regarding membrane selectivity, separation factor was calculated based on water content, which was the highest in feed stream. Both separation and enrichment factors for acetone were higher than the ones for butanol. For both components, the highest separation factors were noticed for the intermediate condition, which seems to be the most interesting one, since the flux is higher and so is the organic content and butanol concentration. However, another pervaporation step for water removal might be necessary depending on the final application.

Permeability was calculated for acetone and butanol in each test condition. The results are presented in Figure 2. The permeability of acetone was decreased with the increase of its content on the feed stream, while butanol permeability reached a maximum in an intermediate concentration. This indicated that the transport mechanisms of these two species are different. In addition to it, the sorption-diffusion model does not apply, since it would be expected an increase of permeability with feed content. These can be ascribed to the presence of the filler in the membrane.

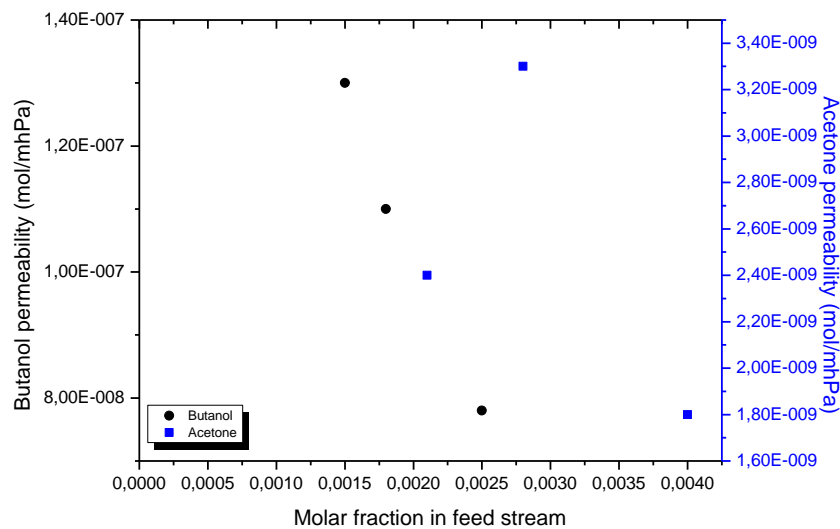


Figure 2: Permeability results for acetone and butanol as a function of its content in feed stream.

It is worth noting that the selected membrane showed the highest free fraction volume and pore concentration compared to other filler contents of 0, 0.5 and 2 wt % [5]. Therefore, it was not expected differences in diffusion coefficients of the same specie with feed content. Also, previous work showed that the increase in temperature of the test favored butanol permeation, which could be ascribed to the energy used for its desorption from activated carbon. Probably, the permeability behavior can be due to a specific adsorption of acetone, butanol and even ethanol, although this last specie was not detected in the permeate stream. Probably, the 4 hours of permeation was not sufficient to establish a steady state permeation of the system. A comparative study of possible competition between acetone, butanol and ethanol in activated carbon might show this behavior. It will be investigated in further studies. However, the swelling of the membrane in pure acetone, ethanol and butanol were determined. The results of weight increase as a function of time and activated carbon are shown in Table 2.

Table 2: Swelling results of acetone, butanol and ethanol in the membranes with varying activated carbon content

Solvent	Activated carbon (wt%)	Weight increase (%)		
		24 h	48 h	72 h
Acetone	0	6.7	7.0	6.9
	1	8.1	7.8	9.0
	2	7.6	8.2	8.4
	3	8.4	8.4	9.0
Butanol	0	6.1	6.8	7.0
	1	7.3	7.8	8.1
	2	5.4	5.3	5.6
	3	5.8	6.6	6.9
Ethanol	0	0.7	0	0
	1	1.3	1.8	2.3
	2	1.5	1.7	1.8
	3	1.1	2.2	2.2

The addition of activated carbon increased the swelling degree of all species, although there was no linearity between the filler content and swelling. In general, the swelling of the membranes in the following sequence: acetone > butanol > ethanol. It was also observed that changes in swelling with time were significant for both acetone and butanol, confirming the hypothesis of non-steady state conditions in pervaporation tests (4 hours). Besides, the addition of activated carbon content did increase the time to attain equilibrium, probably due to the tortuosity of diffusion path inside the membrane. At least, the increase in free fraction volume for the membrane with 1 wt% of the filler was corroborated by higher swelling degree for butanol and acetone.

Regarding the behavior of ethanol, not detected in permeate, it was shown in Table 2 the small swelling degree in pure PDMS (virtually null). The addition of activated carbon increased the swelling, but in low content. The adsorption of ethanol in AC also showed a low value, as described in another paper [12]. The adsorbed amount, q , is much lower for ethanol, compared to butanol and acetone, probably due to the high polarity of the solvent.

4. CONCLUSION

The results showed that activated carbon changed the affinity of the PDMS membrane to butanol, acetone and ethanol. It was not possible to ascribe the transport behavior to sorption in the polymer, transport through the filler or diffusion in the membrane. It seems that both adsorption and filler tortuosity modified the permeation results. Swelling of pure species indicated that during 4 hours of permeation tests might not be enough to attain steady state transport.

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