



## Valorization of brewer's spent grain by furfural recovery/removal from subcritical water hydrolysates by pervaporation

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### ABSTRACT

This work is focused on the development of a sustainable process for the valorisation of the main by-product generated in the brewing industry, the brewer's spent grain (BSG). A two-step process combining subcritical water treatment and pervaporation (PV) was proposed to hydrolyse the hemicelluloses fraction of this lignocellulosic biomass and further removal/recovery of some of the degradation products of sugars by using two different organophilic membranes, polydimethylsiloxane (PDMS) and polyoctylmethylsiloxane (POMS) membranes. Specifically, furfural is the dehydration product of pentoses and it is one of the top biomass-based chemicals being an important platform chemical. For synthetic binary mixtures, lower total permeation flux but higher enrichment factors for furfural were determined for POMS. When dealing with subW hydrolysates, POMS membranes yielded the highest furfural recovery, 94.1 %, with permeate concentrations as high as 40 g·L<sup>-1</sup>. Furthermore, it was assessed that PV is a suitable detoxification method that yielded a retentate nearly free of furfural allowing its use as growth media in the opposite to the subW hydrolysate with inhibitory furfural concentrations for microbial bioprocesses.

### 1. Introduction

Lignocellulosic biomass is one of the most attractive options to achieve sustainable production of energy and chemicals as substitutes for petroleum-based products. The generation of lignocellulosic biomass by different industries is encouraging the implementation of a bio-refinery approach to obtain different valuable products from one residue stream. The brewing industry generates different by-products during beer production, being the most important the solid residue generated after the mashing and wort filtration processes the brewer's spent grains (BSG) accounting about 85 % of the total by-products [1].

BSG presents a valuable chemical composition with a high content of protein and carbohydrates and is a significant source of phenolic compounds [2,3]. Among the different technologies proposed to valorize lignocellulosic biomass, the use of subcritical water (subW) has been growing attention to fractionate the biomass into its individual building blocks by hydrolysis [4]. Subcritical water is water in its liquid state in the temperature range from 100 °C up to 374 °C, its critical temperature.

Increasing temperatures in the subcritical state lead to higher ionic products, lower densities and dielectric constants than under ambient conditions. The incorporation of lignocellulosic biomass into the bio-refinery concept involves the separation and recovery of valuable compounds generated during the entire processing. In this regard different membrane separation processes have gained particular interest for bioenergy and biomaterials production [5]. Membrane technologies are environmentally friendly, low energy consuming and easy to scale up. Pervaporation is a membrane separation process that has been proposed to remove and recover some of the compounds generated during the acidic hydrolysis process of biomass [6,7]. Pervaporation uses non-porous membranes to separate a mixture of liquids by vaporization of the permeate phase. The mass transport through the membrane involves three steps: sorption, diffusion of the components through the membrane and desorption by evaporation at the permeate side. The driving force of the process is usually obtained by lowering the pressure on the permeate side of the membrane. The main advantage of the pervaporation process is that the selectivity of the process can be

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optimized by choosing the appropriate membrane material. By using specific organophilic membranes, hydrophobic solutes may be sorbed in the non-porous membrane and diffuse across the membrane [5].

The selectivity of PV membranes can be crucial considering a double objective. On the one hand, inhibitors from lignocellulosic subW hydrolysates should be removed for allowing its further use as fermentation broths, such as furan derivatives and some short chain organic acids. On the other hand, according to the circular economy model, separation and purification of these bio-based chemicals is important for producing chemical compounds with enough purity. Biomass rich in hemicelluloses, such as BSG, is a source of furan derivatives such as furfural which is one of the main degradation products of the hemicellulose fraction. Furfural has recently been emphasized as one of the top value-added chemicals derived from biomass which can be used to produce more than 1600 kinds of chemical products [8,9]. Conventional processes for furfural separation are distillation, steam stripping, adsorption of liquid–liquid extraction. However these methods are energy and time-consuming and usually involve the use of harmful organic solvents. According to Shan et al. [9], despite the great potential of PV in furfural recovery, related studies are barely reported. Terblanche [7] proposed the recovery of acetic acid and furfural from an acidic hydrolysate coming from steam treated wood by using a polydimethylsiloxane membrane (PDMS) and a polyether block amine (PEBA) membrane. PDMS provided better separation of acetic acid and furfural from the acidic hydrolysate due to interaction between PEBA membrane and the organic compounds generated in the acidic hydrolysates. Cai et al. [10] proposed the use of PDMS pervaporation membrane for the detoxification of sweet sorghum bagasse hydrolysate obtained by using dilute acetic acid as well as the subsequent removal of butanol generated during the hydrolysate fermentation. Significant reduction of furfural from the hydrolysates was obtained achieving a 94.5 % of furfural removal. All these studies proposed the use of dilute acetic acid to obtain the acid hydrolysates of the different biomasses. These and other different hydrolysates coming from low cost lignocellulosic biomass sources can be potential suitable substrates for high value added products' bioprocesses if microbial inhibitors are removed.

This work discusses the use of organophilic pervaporation membranes for the removal and recovery of furfural, and other organic compounds produced as degradation products from subcritical water hydrolysates of brewer's spent grain, specifically the use of PDMS and polyoctylmethyl siloxane (POMS). According to our knowledge no previous results regarding the use of POMS membranes have been found in the literature for furfural recovery. However, POMS is one of the most common materials for organic compounds separation, such as ethanol, butanol, acetone or ethyl acetate [11–13]. Therefore, this membrane material has been also chosen as organophilic membrane to remove sugar-derived compounds formed in subW hydrolysates of BSG. Results will be presented in terms of permeate flux, enrichment factor and performance separation index. PV separation process was also evaluated as an effective detoxification method for removing inhibitors, such as furfural, leaving the sugars of the hydrolysates available for subsequent microbial bioprocesses.

## 2. Experimental section

### 2.1. Materials

#### 2.1.1. Raw material

The raw material used in this work was the brewer's spent grain supplied by San Miguel S.A. This raw material was first preconditioned, as soon as received, by washing and drying it in an air convection oven (45 °C) until reaching a final moisture content of 8 % (w/w). Dehydration was necessary to minimize microbial spoilage. The dry BSG was milled in a Retsch SM100 mill by using an aperture size of 0.5 mm. The particle size distribution was determined by a vibratory sieve shaker (CISA RP.09), with the following mass percentage distribution: >1 mm,

5.2 %; 1–0.5 mm, 52.2 %; 0.5–0.25 mm, 28.5 %; 0.25–0.125 mm, 8.7 % and < 0.125 mm 1.7 %.

Biomass characterization was performed according to the NREL protocols [14]. Carbohydrates were quantified by high-performance liquid chromatography (HPLC) with a Bio-Rad Aminex-HPX-87H column, a variable wavelength detector (VWD) and a refractive index detector (RID) using a mobile phase constituted by 0.005 M sulphuric acid. The column detector was maintained at 40 °C. Megazyme Total Starch Assay (amyloglucosidase/ $\alpha$ -amylase method) was followed to determine starch in the BSG. Additionally  $\beta$ -glucans content was performed using Megazyme  $\beta$ -Glucan Assay Kit (Mixed Linkage). Protein in the raw material was estimated from the nitrogen content present in the samples by performing the elemental analysis (Thermo Scientific Model Flash 2000) and considering a nitrogen factor of 6.25 according to Alonso-Riaño et al. [2]. The oil content of the BSG was determined by Soxhlet extraction (Buchi B-8111) using hexane as solvent.

#### 2.1.2. Pervaporation membranes

Two different organophilic dense membranes were kindly provided by Helmholtz-Zentrum Hereon (Germany) and tested in this study: (1) a membrane whose active layer was based on polydimethylsiloxane (PDMS) (2) another membrane whose selective layer was based on polyoctylmethyl siloxane (POMS).

### 2.2. Subcritical water hydrolysis

Subcritical water hydrolysis treatment was carried out in a laboratory-scale discontinuous stainless-steel reactor of 0.5 L maximum capacity. The heating system used to reach the working temperature consisted of a heating jacket (230 V and 400 W) covering the reactor. A Pt100 sensor connected to a PID system and placed inside the reactor helped to control and register the temperature during the hydrolysis. In a hydrolysis, experiment biomass was loaded into the reactor and filled with water. The mixture was heated up to the desired temperature, and pressure was fixed at 50 bar by using nitrogen gas and maintained during all the process. subW hydrolysis was carried out at 175 °C for a total treatment time of 60 min and a biomass loading of 5 % (w/v). The final hydrolysate was allowed to cool and was subjected to further analysis.

### 2.3. Pervaporation experiments

Pervaporation equipment and performance was previously described elsewhere [15,16]. The pervaporation equipment consisted of a feed tank, a peristaltic pump and a plate and frame laboratory stainless steel permeation cell (Sulzer Chemtech®), with an effective membrane area of 170 cm<sup>2</sup>. This system provides a feed radial flow over the membrane surface. The temperature of the feed liquid mixture was kept constant ( $\pm 1$  °C) by means of a thermostat to heat the jacketed stirred tank feed reactor. The feed flow rate was set to 70 kg·h<sup>-1</sup>. In the permeate side, the permeate was condensed on two parallel glass cold traps cooled by liquid nitrogen to ensure all the permeate was collected. Permeate pressure was kept constant at  $3 \pm 2$  mbar by using a vacuum pump (Edwards RV12) and a vacuum controller (CVC-3000).

Two types of pervaporation experiments were carried out for each type of membrane. First, steady state pervaporation experiments were carried out for synthetic water solutions of the pure compounds by using a feed tank of 5 L capacity. This way, due to the small amount of permeate product, the concentration of the compounds in the feed tank was kept approximately constant along the operation. Pervaporation experiments for pure components were performed at different temperatures in the range of 30 to 59 °C and different feed compositions with pure acetic, formic and levulinic acids, furfural and hydroxymethyl furfural. Finally, pervaporation of subW hydrolysates was carried out under unsteady state operation, at constant temperature of  $55.5 \pm 0.5$  °C by using a smaller feed tank reactor (0.5 L) to increase the ratio of

membrane area to initial feed volume allowing to observe the decrease in compounds present in the hydrolysates that would preferentially permeate through the membrane.

Organic compounds flux was calculated from the total permeation flux and the mass fraction of the component in the permeate:

$$J_i = J_{tot} \cdot w_i \quad (1)$$

where  $J_{tot}$  and  $J_i$  are the total and individual permeation flux, in  $\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ , and  $w_i$  is the concentration of component  $i$  in the permeate, expressed as weight fraction.

The chemical stability of the membrane was checked periodically by measuring the pure water permeation flux at reference operating conditions. The separation performance of the pervaporation membranes was checked by the enrichment factor ( $\beta$ ), defined for a specific component as the relationship between its concentration in the permeate and the feed:

$$\beta = w_{i,p} / w_{i,f} \quad (2)$$

The performance of PV membranes was also evaluated through the pervaporation separation index, PSI, which is the tradeoff relationship between permeation flux and separation factor [17]:

$$\text{PSI} = J_{tot} \cdot \beta \quad (3)$$

#### 2.4. Microbial culture and bioprocess

The detoxified subW hydrolysate obtained after pervaporation to remove the furfural was tested as a growth medium to *Spathaspora passalidarum* bioprocess. *S. passalidarum*. CBS 10,155 (NRRL Y-27907) yeast was purchased from the Westerdijk Fungal Biodiversity Institute (Utrecht, The Netherlands) and handled with sterility. This strain was grown at 28 °C and maintained at 4 °C on Petri dishes with solid yeast medium (YM) composed of 3.3 g·L<sup>-1</sup> glucose, 6.7 g·L<sup>-1</sup> xylose, 5 g·L<sup>-1</sup> peptone, 3 g·L<sup>-1</sup> malt extract, 3 g·L<sup>-1</sup> yeast extract, and 20 g·L<sup>-1</sup> agar. Pre-inoculum was prepared by transferring a colony from a maintenance YM Petri dish to 5 mL liquid YM (similar to solid YM, except for agar) and was incubated at 28 °C and 180 rpm for 24 h. The inoculum was prepared by transferring the pre-inoculum to 20 mL of fresh liquid YM. The inoculum was incubated at 28 °C and 180 rpm for 14 h. All these procedures were carried out in duplicate.

Bioprocess assays were carried out in duplicate using 100 mL Erlenmeyer flasks with a working volume of 25 mL, incubated at 28 °C and 180 rpm. Supplementation was composed of 2.0 g·L<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, 1.0 g·L<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.5 g·L<sup>-1</sup> MgSO<sub>4</sub>·7H<sub>2</sub>O, and 2.5 g·L<sup>-1</sup> yeast extract. These components were dissolved directly in the hydrolysates to avoid sugars dilution. The growth media contained 90 % (v/v) hydrolysate, and the exact volume of inoculum, which guarantees an OD<sub>620</sub> nm of about 0.400. The final volume of each hydrolysate was adjusted with a NaCl solution (0.9 % w/v). Samples were withdrawn during the assays. Biomass was monitored by measuring optical density at 620 nm (UVmini-1240, Shimadzu, Tokyo, Japan) and converted into concentration using a calibration curve. The pH was monitored by using an electrode InPro 3030/200 (Mettler Toledo, Columbus, OH, USA) connected to a benchtop meter sensION + MM340 (Hach, Loveland, CO, USA).

Bioprocess assays were carried out for evaluating yeast performance on the subW hydrolysates, before and after pervaporation, to study the effect of pervaporation inhibitors removal from the subW hydrolysates.

#### 2.5. Analytical methods

Identification and quantification of the hydrolysed polysaccharides fraction and its degradation products were performed by HPLC following the same method as for biomass characterization and described in section 2.1.1. Monosaccharides and degradation products were directly analyzed in the samples previously filtered through a 0.22

µm pore size syringe filter (Scharlab). The standards employed for the HPLC analysis were glucose (99.5 %), xylose (99 %), arabinose (99 %) and furfural (99 %) purchased from Sigma Aldrich (Spain). An aqueous lactic acid solution (20 %) was purchased from Acros, formic acid (98 %) was purchased from Fluka, 5-hydroxymethylfurfural (97 %) was purchased from Alfa Aesar, acetic acid (99.8 %) was purchased from VWR Chemicals and levulinic acid (98 %) from Merck.

### 3. Results and discussion

#### 3.1. Biomass characterization

The chemical composition of the BSG employed in this work is presented in Table 1 in a weight percentage dry basis. The extractive compounds accounted for 14.5 ± 0.2 % (w/w) (with values of 9.2 ± 0.1 and 5.3 ± 0.1 for water and ethanol soluble fraction, respectively). Total protein content was 22.1 ± 0.5 % (w/w) and the lipid fraction was 6.2 ± 0.3 % (w/w). The main polysaccharide fraction was hemicellulose, with 32.0 ± 0.6 % (w/w), followed by the cellulose fraction, 14.0 ± 0.2 % (w/w).

#### 3.2. Subcritical water treatment of BSG in a discontinuous reactor

Subcritical water treatment was performed at 175 °C with a biomass loading of 5 % (w/v) for a treatment time of 60 min. After cooling, the hydrolysates were filtered and analyzed. Hydrolysis was performed in duplicate, and the composition of the two batches is presented in Table 2. Hydrolysates were a complex mixture of different organic compounds. A similar composition was obtained for both subW batches; however, the detailed composition was presented for each run since they were used as initial feed for different pervaporation experiments with PDMS and POMS membranes, immediately after subW hydrolysis to avoid further degradation of the compounds along time which might take place even under refrigeration conditions. According to the chemical composition of subW hydrolysates, the main monomeric sugar released to the medium was xylose. Sugars degradation products were also determined in the hydrolysates, being the main compound furfural from pentoses dehydration reactions (from 1.3 to 1.7 g·L<sup>-1</sup>). In subW hydrolysates organic acids were also determined, being acetic and formic acids, the major organic acids found.

#### 3.3. Evaluation of PDMS and POMS membranes performance with synthetic solutions of pure compounds

Pervaporation performance of some of the sugar degradation

**Table 1**  
Chemical composition of BSG expressed in weight percentage in a dry basis.

Component	g/100 dry-BSG
Extractives in water	9.2 ± 0.1
Extractives in ethanol	5.3 ± 0.1
Protein*	22.1 ± 0.5
Cellulose	14.0 ± 0.2
Starch	4.10 ± 0.06
β-Glucan	0.99 ± 0.01
Hemicellulose	32.0 ± 0.6
Xylan	21.6 ± 0.4
Arabinan	9.5 ± 0.4
Acetyl groups	0.93 ± 0.05
Soluble lignin	5.3 ± 0.2
Insoluble lignin	15.5 ± 0.1
Lipids	6.2 ± 0.3
Ash	3.32 ± 0.06

\* Protein includes the protein content in the extractives fraction. Values are expressed as mean ± standard deviation from duplicate determinations.

**Table 2**

Composition of subcritical water hydrolysates of BSG used as feed composition in pervaporation experiments ( $C_{o,PDMS}$  and  $C_{o,POMS}$ ) and after pervaporation  $C_{PV,PDMS}$  and  $C_{PV,POMS}$  ( $g \cdot L^{-1}$ ).

Compound		$C_{o,PDMS}$	$C_{PV,PDMS}$	$C_{o,POMS}$	$C_{PV,POMS}$
Glucose	Monomer	0.35	0.44	0.35	0.37
Xylose	Monomer	1.51	1.79	1.47	1.53
Arabinose	Monomer	0.28	0.34	0.28	0.30
Other compounds	Furfural	1.7	0.35	1.3	0.17
	HMF	0.18	0.20	0.15	0.16
	Formic acid	0.46	0.55	0.36	0.41
	Acetic acid	0.85	0.89	0.79	1.0
	Lactic acid	0.27	0.32	0.30	0.31
	Levulinic acid	–	0.03	0.032	0.033
	Succinic acid	0.35	0.50	0.43	0.45

compounds determined in the subW hydrolysates was first considered. Subsequently, PV of subW hydrolysates from BSG was studied.

### 3.3.1. Effect of temperature on pervaporation performance

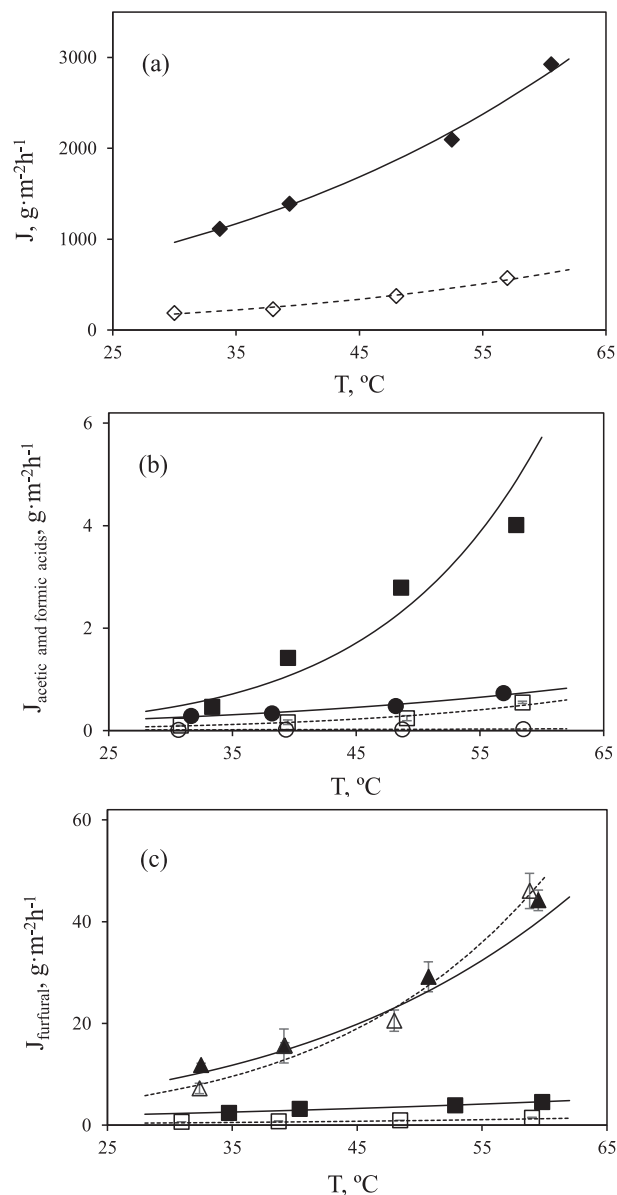
The effect of temperature on flux and selectivity was studied by varying the working temperature in the range from 30 to 59 °C at a fixed permeate pressure of 300 Pa. The pervaporation experiments were carried out for pure water, and different dilute synthetic organic mixtures of pure compounds determined as degradation products from sugar monomers in the subcritical water hydrolysates (see Table 2): furfural, acetic acid, formic acid, levulinic acid and hydroxymethyl furfural.

Fig. 1 shows the water and organic compounds permeation flux determined for PDMS and POMS membranes at different temperatures. The total permeation flux of organic model solutions was of the same order as the pure water permeation flux due to the low concentration of the organic compounds in the feed. Total and individual permeation flux increased exponentially with temperature for both membranes in the temperature range covered in this work, due to the increase in the driving force of the process; although, higher permeation flux was obtained for PDMS than for POMS membrane due to a high mobility of the shorter polymer chain of PDMS compared to POMS. The effect of temperature on permeation flux was described by an Arrhenius type equation:

$$J_i = J_{i,o} \exp\left(-\frac{E_{a,i}}{RT}\right) \quad (4)$$

where  $J_i$  is the permeation flux ( $g \cdot m^{-2} \cdot h^{-1}$ ),  $E_{a,i}$  is the apparent activation energy of permeation ( $kJ \cdot mol^{-1}$ ),  $R$  is the ideal gas constant,  $J_{i,o}$  is the preexponential factor, and  $T$  is the absolute temperature. Apparent activation energies were calculated from the slope of  $\ln J$  versus  $T^{-1}$  plot and are listed in Table 3. The positive values of the apparent activation energy indicated that an increase in temperature increased water and organic permeation flux. By increasing temperature, the driving force increased due to the increasing vapour pressure. Additionally, an increase in temperature caused an increase in the motion of the polymer chains, improving the diffusion of the permeant molecules [15,16]. Similar values of apparent activation energy of water permeation were obtained for PDMS and POMS membranes, showing a similar temperature sensitivity, although higher water permeation flux was obtained for the PDMS membrane. Terblanche [7] reported a similar value for water activation energy through a PDMS membrane  $34 \pm 2 kJ \cdot mol^{-1}$ . However, higher values for the apparent activation energy of water through PDMS and POMS membranes were also found in the literature, with values of 43.5–46.7 and 42.5–46.65  $kJ \cdot mol^{-1}$  for POMS and PDMS membranes, respectively [13,15,16,18].

Among the different organic compounds explored in this work, acetic acid and furfural (at their highest concentration level studied) showed the highest sensitivity towards a temperature increase. A higher value of the apparent activation energy indicated a more sensitive behavior to-



**Fig. 1.** Permeation flux of synthetic mixtures as a function of temperature (a)  $\blacklozenge$   $\blacklozenge$  water (b)  $\blacksquare$   $\blacksquare$  acetic acid (1 g/L) and  $\bullet$   $\circ$  formic acid (0.35 g/L) and (c) furfural  $\blacksquare$  0.17 g/L  $\square$  0.15 g/L  $\blacktriangle$  1.7 g/L and  $\triangle$  1.5 g/L. Filled symbol PDMS membrane open symbols POMS membrane. Lines represent the Arrhenius relationship.

**Table 3**

Apparent activation energies ( $E_{a,i}$   $kJ \cdot mol^{-1}$ ) for water, acetic acid, formic acid and furfural through PDMS and POMS membranes.

Component	PDMS	POMS
Water	$30 \pm 1$	$35 \pm 3$
Acetic acid 1.0 $g \cdot L^{-1}$	$77 \pm 15$	$51 \pm 6$
Formic acid 0.35 $g \cdot L^{-1}$	$31 \pm 3$	$20.3 \pm 0.7$
Furfural 0.17–0.15 $g \cdot L^{-1}$	$20 \pm 3$	$23 \pm 3$
Furfural 1.7–1.5 $g \cdot L^{-1}$	$42 \pm 2$	$55 \pm 7$

ward temperature changes, inferring that, for both compounds, permeation flux is more dependent on temperature than water permeation. Other values reported in the literature for the apparent activation energy of these compounds through PDMS membrane were  $22.5 \pm 9.5$  and  $45.6$

$\pm 4.5 \text{ kJ}\cdot\text{mol}^{-1}$  for acetic acid (feed concentration of  $4.8 \text{ g}\cdot\text{L}^{-1}$ ) and furfural (feed concentration of  $1 \text{ g}\cdot\text{L}^{-1}$ ), respectively, while no data were found for POMS membrane. In the case of hydroxymethyl furfural and levulinic acid organic permeation flux was negligible due mainly to the low vapour pressure of these compounds and the low concentration level determined in the subW hydrolysate ( $p_{\text{HMF}60^\circ\text{C}}^0 = 0.0026 \text{ kPa}$ ,  $p_{\text{levulinicacid}60^\circ\text{C}}^0 = 0.033 \text{ kPa}$  [19,20]).

To evaluate the selectivity of each membrane towards the different organic compounds the enrichment factor ( $\beta$ ) and the PSI were evaluated at different temperatures (Fig. 2). An increase in temperature induced an increase in the diffusivity of the organic compounds through the polymer membrane, increasing the enrichment factors in the case of POMS membrane. However this effect was not clearly observed for PDMS membrane. For PDMS and POMS, membranes the enrichment factors obtained for organic acids were lower than the unity since lower concentrations of organic acids were determined in the permeate than in the feed. Terblanche [7] obtained similar results regarding the selectivity of PDMS membranes towards acetic acid when worked with a feed concentration of  $4.6 \text{ g}\cdot\text{L}^{-1}$ , with an enrichment factor of about 0.2 at  $80^\circ\text{C}$ . However, other studies showed that PDMS membranes were slightly more selective towards acetic acid than water when the acetic acid concentration was much higher in the feed,  $100 \text{ g}\cdot\text{L}^{-1}$  [21]. Therefore, it could be concluded that the organic acid concentration in the feed may play an important role regarding the selectivity of the membranes.

On the other, hand for PDMS and POMS, membranes the enrichment factors obtained for furfural were higher than the unity due to higher furfural concentration in the permeate than in the feed. As it can be observed in Fig. 2c and 2d, the furfural enrichment factors were higher for POMS than for PDMS membranes which, could be attributed to the incorporation of a longer chain alkyl group in POMS that leads to a higher degree of hydrophobization of the membrane material, which resulted in an increase of the furfural sorption, enhancing the subsequent diffusion through the membrane. For PDMS membrane,

Terblanche [7] showed lower enrichment factors for furfural than the values reported in this work, with values between 1.4 and 2.1 in the temperature range from  $40$  to  $80^\circ\text{C}$  and for a furfural feed concentration of  $1 \text{ g}\cdot\text{L}^{-1}$ . The furfural enrichment factors for the POMS membrane greatly increased with temperature, especially at the highest furfural concentration level assayed in this work,  $1.5\text{--}1.7 \text{ g}\cdot\text{L}^{-1}$ . The increase of furfural selectivity with temperature for POMS membranes was probably due to a higher diffusion increase with temperature for furfural than that of water. Similarly, Ghosh et al. [22] also observed an increase in furfural concentration in the permeate with temperature when using a furfural feed concentration of 2 wt (%) and a polyurethaneurea membrane. These authors expected this behaviour considering that the hydrophobic segments of the membrane interact more with furfural than with water and diffusion of furfural increased more rapidly than that of water with temperature.

To analyze the different affinity of the solutes towards PDMS and POMS membranes the distance parameter between the Hansen solubility parameters of the solute and the polymer was evaluated [23]:

$$R_a = \sqrt{4(\delta_{d,s} - \delta_{d,p})^2 + (\delta_{p,s} - \delta_{p,p})^2 + (\delta_{h,s} - \delta_{h,p})^2} \quad (5)$$

where  $R_a$  is the distance parameter between the solvent (S) and the polymer (P),  $\delta_d$ ,  $\delta_p$ ,  $\delta_h$  are Hansen solubility parameters determining dispersion (d), polar (p), and hydrogen bonding (h) interactions ( $\text{MPa}^{0.5}$ ) respectively. The smaller the  $R_a$  value the stronger interaction between the polymer and the solvent. Hansen solubility parameters and  $R_a$  distance parameters were listed in Table 4.  $R_a$  values were lower for POMS than for PDMS. This agrees with the higher selectivity of furfural found for POMS compared to PDMS but not for the organic acids. According to the distance parameter values, PDMS and POMS membranes should be most selective for acetic acid. However, the highest enrichment factor value determined for both membranes was found for furfural. In this regard, other physicochemical properties of the solvent also play an important role in the pervaporation behavior. Table 4 lists some properties of furfural, acetic and formic acid and water. Although furfural presents the higher molar volume and the lower vapour pressure

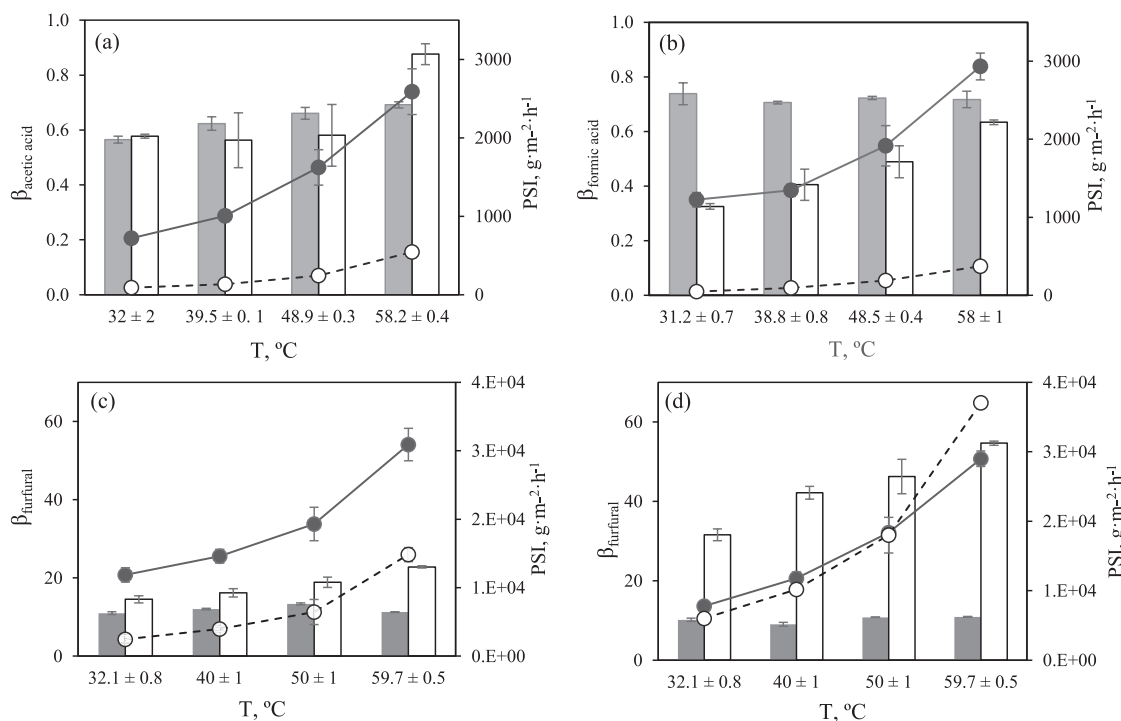


Fig. 2. Enrichment factor –bar graphic–  $\beta$  (■ PDMS □ POMS) and PSI –lines– (● PDMS ○ POMS) determined for each organic compound of synthetic aqueous mixtures (a) acetic acid  $1 \text{ g}\cdot\text{L}^{-1}$ ; (b) formic acid  $0.35 \text{ g}\cdot\text{L}^{-1}$  and furfural at two different feed concentration levels (c)  $0.15\text{--}0.17 \text{ g}\cdot\text{L}^{-1}$  and (d)  $1.5\text{--}1.7 \text{ g}\cdot\text{L}^{-1}$ .

**Table 4**

Hansen's solubility parameters of PDMS, POMS, water, furfural, acetic and formic acids and distance parameter. Physicochemical properties of the solvents.

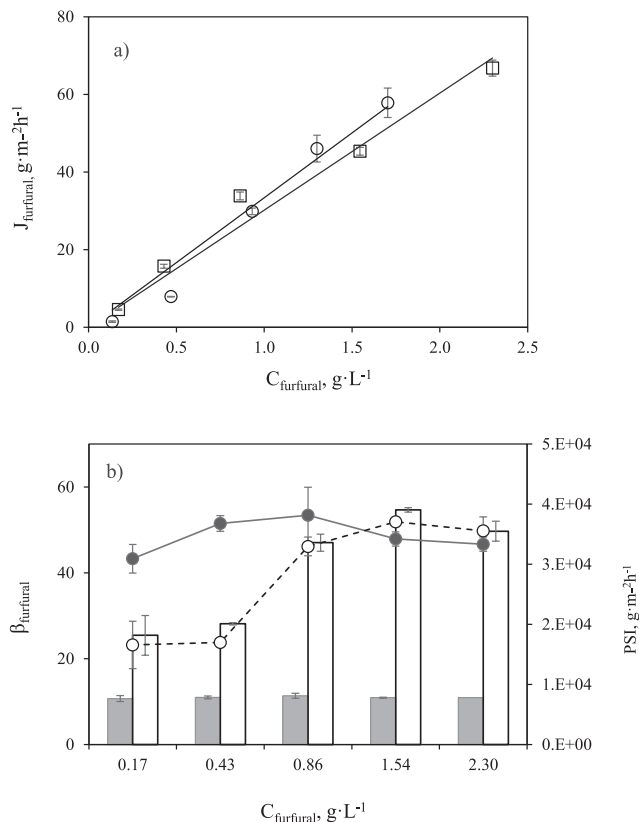
compound	$\delta_d$ (MPa <sup>0.5</sup> )	$\delta_p$ (MPa <sup>0.5</sup> )	$\delta_h$ (MPa <sup>0.5</sup> )	$R_{a,S-PDMS}$ (MPa <sup>0.5</sup> )	$R_{a,S-POMS}$ (MPa <sup>0.5</sup> )	$V_m$ (cm <sup>3</sup> mol <sup>-1</sup> )	$p^o$ (kPa) at 30/60 °C	log $K_{ow}$	Reference
PDMS	15.9	0	4.1						[13]
POMS	14.8	5.6	6.5						[13]
Water	15.5	16.0	42.3	41.4	37.3	18.1	4.3/19.9	-1.38	[23,33]
Furfural	18.6	14.9	5.1	15.9	12.1	82.9	0.4/2.3	0.41	[23,33]
Acetic acid	14.5	8	13.5	12.7	7.4	57.2	2.8/12.1	-0.17	[23,33]
Formic acid	14.3	11.9	16.6	17.6	12.0	37.7	7.2/22.0	-0.54	[23,33]

values, it presents the higher octanol/water partition coefficient (log  $K_{ow}$ ). Positive values for log  $K_{ow}$  indicate some hydrophobic character, and larger values show more hydrophobicity. Molecules with low or negative values for log  $K_{ow}$  are frequently indicated as polar. Based on the results obtained in this work for PDMS and POMS membranes, this parameter seems to play an important role in the pervaporative behaviour of some of the chemical compounds determined in subcritical water hydrolysates.

As it was previously described, PDMS membranes showed higher total permeation flux but lower enrichment factors for furfural than POMS membranes. Therefore, to consider the overall performance of the membrane, the PSI was also calculated. As a general trend, the PSI for all the organic compounds studied in this work increased with temperature. For organic acids, PSI for POMS membranes were lower than for PDMS membranes due to the higher total permeation flux through PDMS, while enrichment factors were of the same order for both membranes. For furfural, PSI was higher for PDMS than for POMS membrane at the lowest furfural feed concentration assayed in this work, 0.15–0.17 g L<sup>-1</sup>. However, by increasing feed concentration, PSI for furfural was of the same order for both membranes, even higher for POMS at the highest temperature assayed in this work, due to a higher enrichment factor that compensated the lower total permeation flux. The higher the PSI, the more efficient the membrane used in pervaporation to recover a targeted compound. Therefore, POMS membrane was found a suitable material to selectivity recover furfural at concentrations initially found in subcritical water hydrolysates.

### 3.3.2. Effect of furfural concentration in the feed

According to the results presented in section 3.3.1, furfural is the main degradation compound from sugar in subW hydrolysates that could be selectively removed by PV. In a non-steady PV process, furfural concentration in the feed won't be constant due to its selective removal by PV. Therefore, the effect of the furfural feed composition on furfural permeate flux, enrichment factor and PSI was studied in the concentration range from 0.15 to 2.2 g L<sup>-1</sup> at 59 °C for both types of membranes. By increasing the furfural concentration in the feed, the furfural permeation flux increased, showing a linear relationship between furfural permeation flux and furfural feed concentration (Fig. 3); although the total permeation flux did not change significantly due to the low furfural concentration in the feed. By increasing the furfural concentration in the feed, sorption of furfural was higher and diffusion through the membrane was enhanced, resulting in a higher furfural permeation flux. Quin et al. [8] also found an increase in furfural permeation flux by increasing its feed concentration in the feed concentration range from 0.5 to 6.5 wt (%) at different temperatures (from 35 °C to 80 °C) for PDMS membranes. These authors explained that the increase in furfural feed concentration tended to facilitate the dissolution of furfural in the membrane, which would increase the swelling degree of the membrane; as a result, the free volume of the membrane was enhanced, leading to a decrease in the mass transfer resistance of furfural. These authors also found that water flux was relatively constant by increasing the furfural feed concentration, although higher total permeation flux was obtained due to the increase of furfural permeation flux. Ghosh et al. [22] also observed a rise in furfural permeation flux and total permeation flux with increasing furfural concentration in the



**Fig. 3.** (a) Furfural permeation flux as a function of furfural feed concentration of synthetic aqueous mixtures ( $\square$  PDMS membrane  $J_{furfural} = 30.17 C_{furfural,feed}$ ,  $R^2 = 0.9676$ ;  $\circ$  POMS  $J_{furfural} = 33.38 C_{furfural,feed}$ ,  $R^2 = 0.9662$ ). (b) enrichment factor  $\beta$  ( $\blacksquare$  PDMS  $\square$  POMS) and PSI ( $\bullet$  PDMS  $\circ$  POMS) for furfural as a function of furfural concentration in the feed.

feed from 2 to 8 wt (%) by using a polyurethane urea membrane. The increase in total permeation flux observed by these authors was related to the so-called bulk flow [22]. This phenomenon was not observed in this work, as the total permeation flux was constant for both membranes due to the lower concentration of furfural in the feed used in this study.

Fig. 3b shows the enrichment factor and PSI for furfural as a function of furfural concentration in the feed. Enrichment factor for PDMS membrane remained more or less constant by increasing the furfural concentration, in the range studied in this work, while it increased until reaching a plateau around 0.86 g L<sup>-1</sup> for POMS membrane. Similar trend was observed for PSI values, with values approximately constant for PDMS membrane; while it increased until reaching a plateau for POMS membrane. Selective layers of both, PDMS and POMS, were built from siloxane; however, PDMS possesses shorter side chain compared to POMS. Long side octyl chains in POMS allow higher sorption affinity for furfural that increased with concentration up to around 0.9 g L<sup>-1</sup> feed concentration. Sorption affinity of PDMS towards furfural was lower than for POMS and it did not show a dependence on furfural

concentration in the concentration range studied in this work. The sorption affinity of furfural for POMS corresponds well to the higher hydrophobicity of long octyl chains and the positive  $\log K_{ow}$  value for furfural.

### 3.4. Pervaporation of subcritical water hydrolysates - permeate and retentate composition

Furfural removal/recovery by PV from subW hydrolysates was studied under unsteady state conditions by using a smaller reactor at a pervaporation temperature of  $55.5 \pm 0.5$  °C, and a permeate pressure of 300 Pa, for both membranes. The initial feed concentration for PDMS and POMS membranes was collected in Table 2.

The total permeation flux for subW hydrolysates was registered along PV experiments. It was observed that, for POMS membrane, the presence of other compounds in the subW hydrolysates did not significantly affect the total permeation flux. However, for PDMS membrane the total permeation flux for subW hydrolysates was lower than the flux observed for diluted synthetic mixtures (around 50 % of total flux drop was observed). Therefore, it could be concluded that for PDMS membrane, the presence of additional components in the subW hydrolysate influenced the permeation flux through the membrane. Similarly, Terblanche [7] observed that, for PDMS membranes, the total permeation flux for acidic hydrolysates was lower than the total permeation flux during the PV of binary mixtures at the same concentration as the acidic hydrolysates ( $4.8 \text{ g}\cdot\text{L}^{-1}$  of acetic acid and  $1 \text{ g}\cdot\text{L}^{-1}$  of furfural). This decrease was more notable at high temperatures. For instance, at 70 °C a total permeation flux around  $1700 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  was obtained for synthetic binary mixtures, while this value was reduced to  $1300 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  in the acidic hydrolysates, indicating a permeation flux decrease of 24 %. However, when PV was performed at 60 °C, the reduction of permeate flux was lower than at 70 °C, around a 14 % decrease. These authors also performed PV of acidic hydrolysate by using a poly(ether-block-amide), PEBA, membrane observing a higher reduction in the total permeation flux than for synthetic dilute mixture compared to PDMS membranes. At 60 °C, the total permeation flux dropped from  $1250 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  for binary dilute mixtures to  $650 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  for the acidic hydrolysate; while, at 70 °C the decrease was even higher at about 68 % from  $2400 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  to  $750 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ . Therefore, based on the findings of this work and the results presented by Terblanch [7], permeation flux decrease for biomass hydrolysates compared to synthetic mixtures in PV depends on the operating temperature and the chemical nature of the membrane.

The chemical composition of the permeate was determined along the PV process. The permeate consisted mainly of water, furfural and small amounts of organic acids for PDMS and POMS membranes. The furfural

concentration in the permeate continuously decreased during PV since furfural concentration in the retentate side decreased along PV time (Fig. 4) due to its selective removal. The furfural concentration in the permeate was higher for POMS membrane than for PDMS membrane, according to the higher furfural selectivity of POMS determined for synthetic mixtures than for PDMS. The furfural percentage recovery in the permeate side is also presented in Fig. 4. It was evaluated considering the permeate volume and furfural concentration in the permeate at the different time intervals analyzed according to Equation 6:

$$\% \text{ Recovery furfural, } R_f = \frac{V_{\text{permeate}} \cdot C_{p,\text{furfural}}}{V_{o,\text{feed}} \cdot C_{f,\text{furfural}}} \cdot 100 \quad (6)$$

where  $V_{\text{permeate}}$  is the volume of permeate in L,  $V_{o,\text{feed}}$  the initial feed volume in L,  $C_{p,\text{furfural}}$  and  $C_{f,\text{furfural}}$  the concentration of furfural in the permeate and in the initial feed respectively in  $\text{g}\cdot\text{L}^{-1}$ .

After 190 min of PV, POMS membrane reached a recovery of furfural of 94.1 %, while 84.4 % was obtained for PDMS membrane at 290 min. The furfural concentration was  $0.35 \text{ g}\cdot\text{L}^{-1}$  and  $0.17 \text{ g}\cdot\text{L}^{-1}$  in the retentates after PDMS and POMS pervaporation, respectively, from initial feed concentrations of  $1.7$  and  $1.3 \text{ g}\cdot\text{L}^{-1}$  (see Table 2), due to its selective removal by PV. The percentage recovery, evaluated from the final furfural concentration in the retentate, yielded values of 80 and 87 % for PDMS and POMS membranes, respectively, which indicates a good mass balance performance with deviations of 5 % and 8 % for PDMS and POMS membranes, respectively. A small control sample of subW hydrolysate was subjected to the same temperature/time conditions as during PV, and furfural concentration did not vary due to chemical reactions.

The concentration of the other components of the subW hydrolysates was also determined in the different permeates collected. However, like for synthetic mixtures, only acetic and formic acids could be determined in the permeate, with negligible amounts of the other compounds present in the subW hydrolysates (see Table 2). Fig. 5 shows the concentration of acetic and formic acids in the permeate. According to the results previously presented, the enrichment factor of both organic acids was less than the unity, as the concentration of these compounds was lower in the permeate than in the initial feed (see Table 2) and remained more or less constant.

The composition of the final retentate after PV was collected in Table 2. Since furfural was the only component that permeated preferentially through the PDMS and POMS membranes, the concentration for the other components (sugar monomers and other organic compounds) of the subW hydrolysates slightly increased after the PV process, due to the removal of water in the permeate side. Greer et al. [6] also indicated that PV leaves the sugars intact and therefore, if water is removed, they

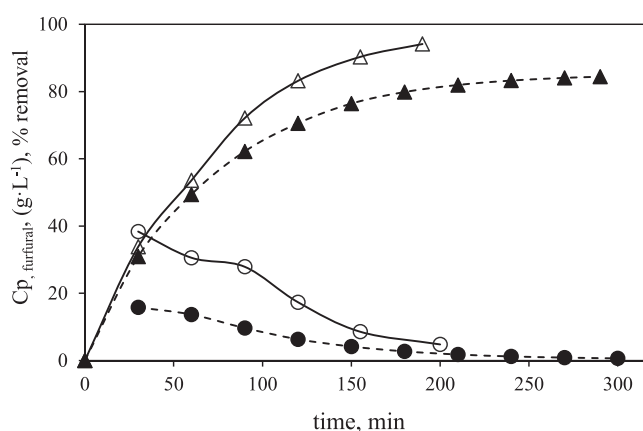


Fig. 4. Furfural concentration in the permeate ( $C_{p,\text{furfural}}$ ) of BSG hydrolysates for each membrane (● PDMS ○ POMS) and percentage removal (▲ PDMS △ POMS) as a function of PV time.

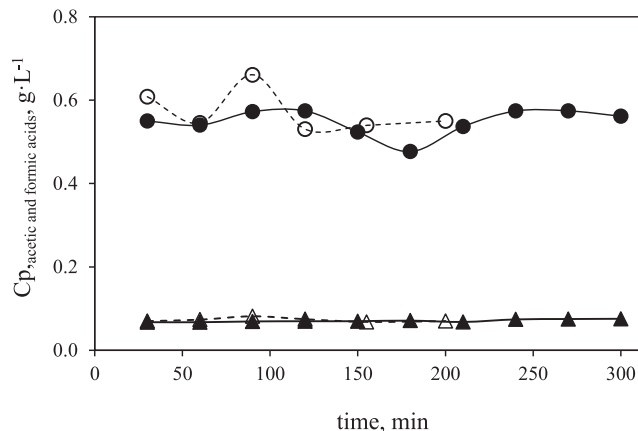


Fig. 5. Concentration of acetic and formic acids in the permeate ( $C_{p,i}$ ) of BSG hydrolysates for each membrane ( $C_{p,\text{acetic acid}}$ : ● PDMS ○ POMS  $C_{p,\text{formic acid}}$ : ▲ PDMS △ POMS) as a function of pervaporation time.

**Table 5**

Comparison of permeates after PV of subW hydrolysates of BSG by PDMS and POMS membranes. Percentage of permeate yield,  $Y_p$ , and furfural recovery,  $R_f$ . Mean concentration values of organic compounds in the permeate  $C_{p,i}$   $\text{g}\cdot\text{L}^{-1}$ .

Membrane	t min	$Y_p$ (%)	$R_f$ (%)	$C_{p,\text{furfural}}$	$C_{p,\text{acetic acid}}$	$C_{p,\text{formic acid}}$
PDMS	210	16.8	81.9	8.5	0.54	0.07
POMS	200	6.0	94.1	20.9	0.57	0.08

should be slightly concentrated in the retentate.

Table 5 summarizes the comparison between the PDMS and POMS performance regarding permeate yield and composition. The comparison was established at a similar PV time of 200 and 210 min for POMS and PDMS membranes, respectively. The final permeate composition in Table 5 was evaluated considering all the permeate volume collected at the selected time. The permeate yield,  $Y_p$ , was calculated according to Equation 7 [24]:

$$Y_p = \frac{\text{mass of permeate}}{\text{initial feed mass}} \cdot 100\% \quad (7)$$

The PDMS membrane presented higher permeation flux, which led to higher permeate yield; however, due to lower values of selectivity for furfural, this membrane also showed lower mean concentration value for furfural considering all the permeate collected ( $8.5 \text{ g}\cdot\text{L}^{-1}$ ). On the other hand, the POMS membrane generated a lower permeate yield but a higher mean concentration value for furfural in the permeate ( $20.9 \text{ g}\cdot\text{L}^{-1}$ ) due to the higher selectivity of the membrane towards furfural, and the lower water permeation flux. The concentrations of the organic acids in the permeate were of the same order for both types of membranes. Based on these results, we can conclude that for efficient removal of furfural, PDMS membrane was a good option since similar furfural recovery was also achieved for the POMS membrane. However, by using POMS membrane, a higher furfural concentration in the permeate was obtained that could be useful for further uses of furfural as a chemical platform in a biorefinery.

Some studies about the PV treatment applied to acid hydrolysates from different biomass sources were found in the literature. Greer et al. [6] hydrolysed *Miscanthus giganteus* with 1.5 % (w/w) of sulfuric acid, at a 25 % (w/w) of biomass loading, at  $190^\circ\text{C}$  for 1 min. The PV processing of the acid hydrolysates containing  $0.69 \text{ g}\cdot\text{L}^{-1}$  of furfural resulted in an aqueous permeate with  $6.3 \text{ g/L}$  of furfural, with a PV separation factor of 8.6, by using a PDMS membrane. Terblanche [7] carried out PV experiments for acid hydrolysate of wood at various temperatures ( $40\text{--}80^\circ\text{C}$ ) with a feed concentration of furfural, formic and acetic acids ( $1.5$ ,  $0.71$  and  $4.58 \text{ g}\cdot\text{L}^{-1}$ , respectively). When using a PDMS membrane, the permeate concentration of each compound varied with the PV temperature in the following ranges: furfural ( $1.32\text{--}3.28 \text{ g}\cdot\text{L}^{-1}$ ), formic acid ( $0.06\text{--}0.09 \text{ g}\cdot\text{L}^{-1}$ ) and acetic acid ( $0.77\text{--}1.43 \text{ g}\cdot\text{L}^{-1}$ ). The highest selectivity of furfural and acetic acid was obtained at  $50$  and  $80^\circ\text{C}$  respectively. The highest furfural and organic acids enrichment factors obtained in that study were  $2.12 \pm 0.07$  and  $0.25 \pm 0.02$ , respectively. However, to the best of the author's knowledge, no pervaporation study has been conducted to investigate the fractionation of subcritical water hydrolysates with organophilic membranes by PV.

### 3.5. Microbial bioprocess of liquid streams from subcritical water treatment before and after pervaporation process

By selective furfural removal from subW hydrolysate through PV, a valuable chemical platform was successfully isolated, and simultaneously a detoxification process was carried out.

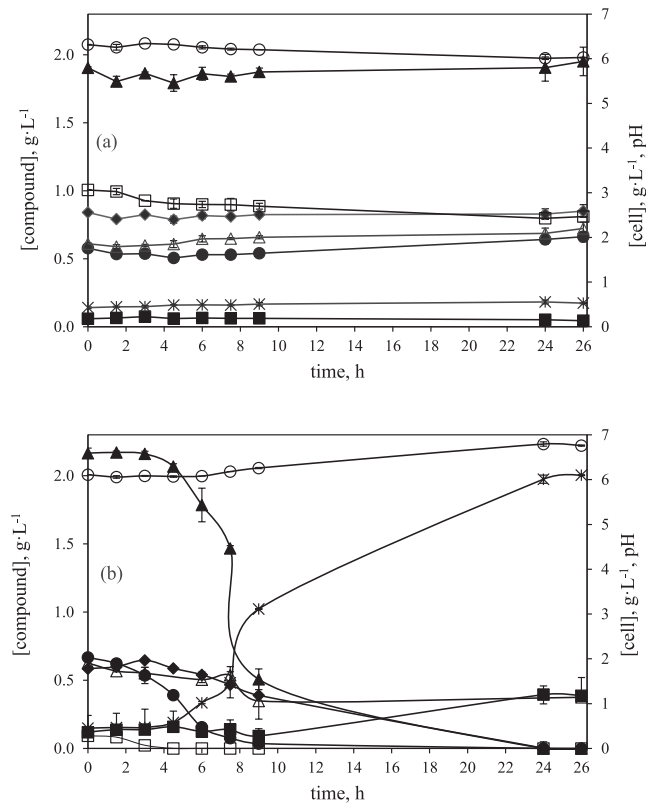
To evaluate the success of this detoxification approach microbial bioprocess assays were carried out by using subW hydrolysates, before and after pervaporation by using POMS membranes. These experiments were carried out at Erlenmeyer flasks using *S. passalidarum*, a native xylose-fermenting yeast with potential to be used for bioethanol

production from lignocellulosic hydrolysates [25,26]. The profiles of cell concentration, glucose, xylose, arabinose, acetic acid and furfural are shown in Fig. 6.

When non-detoxified subW hydrolysate was used (Fig. 6a), no cell growth was detected evidencing that *S. passalidarum* was completely inhibited. In fact, this fermentation broth presented a high ratio of inhibitors to sugars due to the low total sugar concentration. Moreover, it was already described in the literature a synergetic effect of furan derivatives with other toxic compounds (such as acetic acid, formic acid and phenolic compounds among others) even at concentrations below inhibitory level. Therefore, the complete cell growth inhibition observed in this assay was probably due to the synergetic effect of furfural and acetic acid, toxic compounds that reduce drastically cell growth and bioprocess yield [27]. Recently, Vanmarcke et al. [28] studied the major fermentation inhibitors of recombinant 2G yeasts in diverse lignocellulose hydrolysates. The authors concluded that furfural is one of the major inhibitors in all hydrolysates assessed and its presence in a concentration as low as  $0.3 \text{ g/L}$  was enough to reduce fermentation performance. Similar observations were found by Andersen et al. [29], showing that a concentration of furfural above  $0.5 \text{ g}\cdot\text{L}^{-1}$  completely inhibited *Thermoanaerobacter italicus* Pentocrobe 411X growth.

When furfural was almost completely removed from the hydrolysate by PV, *S. passalidarum* was not inhibited, consuming almost all the monomer sugars for cell growth, as shown in Fig. 6b. The lag phase lasted 3 h, when glucose consumption for biomass growth started to be detected. Cell concentration increased exponentially with a specific growth rate of  $0.36 \pm 0.03 \text{ h}^{-1}$  (calculated between 4.5 h and 9 h).

Glucose started to be consumed almost immediately after the beginning of the assay and its exhaustion was detected after 9 h. Until this moment, xylose concentration kept almost constant and a considerable increase in its consumption rate was detected only when almost



**Fig. 6.** Bioprocess assays of the subW hydrolysates with *S. passalidarum*. Evolution of  $\text{pH}$  and concentrations of  $\bullet$  glucose  $\blacktriangle$  xylose  $\blacklozenge$  arabinose  $\blacksquare$  ethanol  $\triangle$  acetic acid  $\square$  furfural and  $*$  biomass ( $\text{g}\cdot\text{L}^{-1}$ ) during the assay. (a) subW hydrolysate (b) subW hydrolysate after PV process.



all the glucose was already exhausted. Xylose concentration decreased considerably between 7.5 h and 9 h, from about  $1.5 \text{ g}\cdot\text{L}^{-1}$  to  $0.5 \text{ g}\cdot\text{L}^{-1}$ . This phenomenon is known as diauxic effect, consisting in glucose preference when the fermentation broth contains both glucose and xylose. Higher rate of xylose consumption was observed only after full consumption of glucose [30]. Arabinose and xylose exhaustion were detected only after 24 h, but certainly it might be occurred significantly earlier given its consumption profile.

Almost all the sugars were consumed for cell growth, achieving a maximum cell concentration of  $6.10 \text{ g}\cdot\text{L}^{-1}$  at the end of the assay (26 h). The cell yield,  $Y_{\text{cell/substrate}}$  ( $\text{g}\cdot\text{g}^{-1}$ ), was calculated according to Equation (8), considering glucose, xylose and arabinose as substrates.

$$Y_{\text{cell/substrate}} = \frac{\Delta[\text{cell concentration}]}{\Delta[\text{substrate}]} \quad (8)$$

The calculated biomass yield was  $1.65 \pm 0.04 \text{ (g}\cdot\text{g}^{-1})$ , indicating that other compounds present in the hydrolysate, such as oligomeric carbohydrates and proteins, may have contributed to the cell growth. A negligible ethanol concentration was detected at the end of the bioprocess since ethanol production was limited by the low initial sugar's concentration. Moreover, some authors already stated that the aeration rate control is one of the most determining parameters to maximize ethanol production from xylose-fermenting yeasts [31,32].

Concluding, these microbial bioprocess experiments showed that detoxification of subW hydrolysates using PV is crucial to ensure proper cell growth through C5 and C6 sugars consumption by *S. passalidarum*. The furfural removal resulted in a short lag phase and reduced significantly the *S. passalidarum* inhibition allowing complete glucose and xylose consumption for cell growth. However, it is crucial to consider these assays as showing the high potential of combining membrane PV-C5-C6 subW hydrolysates detoxification for *S. passalidarum* ethanol fermentation starting with higher initial concentration of sugars in these hydrolysates to ensure their feasibility for the production of bioethanol or other commercial interesting products.

#### 4. Conclusions

Pervaporation has been demonstrated as an efficient technology to be incorporated in a biorefinery process, after the subcritical water pretreatment of BSG.

This work has shown that the selective recovery of furfural, as a biomass-derived platform chemical, from subW hydrolysates could be successfully achieved by pervaporation by using organophilic membranes. PDMS and POMS membranes have demonstrated the ability to remove/recover furfural from the subcritical water BSG hydrolysates, achieving recovery yields of 84.4 % and 94.1, respectively. Furthermore, POMS membrane allowed the recovery of highly concentrated furfural in the permeate.

PV membranes successful removal of furfural, one of the major microbial inhibitors from subW hydrolysates of lignocellulosic biomass, was proven to be a crucial step to ensure microbial cell growth through C5 and C6 sugars consumption by *S. passalidarum*. Detoxification of hydrolysates by pervaporation boosts biorefinery implementation since all the fractions obtained, namely retentate and permeate, enhance process valorization.

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#### CRedit authorship contribution statement

**Patricia Alonso-Riaño:** Conceptualization, Methodology, Investigation, Writing – original draft. **Alba E. Illera:** Data curation, Writing – original draft. **Mariana S.T. Amândio:** Methodology, Data curation. **Ana M.R.B. Xavier:** Supervision, Funding acquisition. **Sagrario Beltrán:** Funding acquisition, Writing – review & editing. **M. Teresa Sanz:** Conceptualization, Supervision, Funding acquisition, Writing – original draft.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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