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Separation of sugarcane bagasse mild alkaline extract components by ultrafiltration – Membrane screening and effect of filtration parameters

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ABSTRACT

Mild alkaline treatment (1.5% NaOH (w/v), solid:liquid ratio of 1:20, 60 °C, 6 h) of sugarcane bagasse (SCB) produced an extract composed of hemicelluloses, lignin, phenolic monomers and acetic acid. The purification of this extract, usually considered a by-product in lignocellulosic biorefineries, is of major importance to give value to the whole mild alkaline fractionation process. Ultrafiltration was assessed to separate the components of the SCB alkaline extract which is a prerequisite for their further valorization. The permeate flux and the retention of the extract components were studied on seven membranes (polysulfone hollow fiber and ceramic tubular) with different molecular weight cut-offs, under various operating conditions. On all the membranes tested, oligomers of lignin and hemicelluloses were separated from salts, phenolic monomers and acetic acid. The 10 kDa polysulfone hollow fiber membrane presented the highest lignin and hemicelluloses retention, exceeding 85 and 90%, respectively, regardless of shear rate and with a limited influence of transmembrane pressure. For salts, acetic acid and phenolic monomers, retention levels of about 0–10% were recorded for this membrane. At 2.8 bar and at 20 °C, the permeate flux reached 16 L/h/m^2 and the critical flux was not reached.

1. Introduction

Lignocellulosic or second generation biorefineries transform agricultural by products or forest biomass into energy, various chemicals and materials [1]. Most lignocellulosic biorefineries currently subject the raw materials to pretreatment with a mineral acid, usually sulfuric acid, to produce monomeric sugars from the cellulose and the hemicelluloses, with lignin mostly recovered in the solid residue of this extraction. Another process gaining importance is the dissolution of the lignin and the hemicelluloses in mildly alkaline conditions, with the recovery of cellulose in the solid residue [2]. Mild alkali based pretreatments originated in the pulp and paper industry, but use less harsh conditions. They yield higher delignification rates and higher total monomeric sugar rates after enzymatic saccharification of the cellulose than acid pretreatments [3,4].

The separation/purification steps are of crucial importance in lignocellulosic biorefineries as they account for 60 80% of the production cost of the end products [5]. For lignocellulosic acid extracts, the monomeric sugars are purified by two chromatographic steps, the first involving the separation of sulfuric acid from the monomeric sugars [6], and the second involving separation of the various sugars from each other [7]. This process is already used industrially by several companies, including BlueFire Renewables (https://bfreinc.com).

For mild alkaline pretreatments, the cellulose remains in the solid residues and the alkaline extracts are considered to be the by products of the biorefinery. Lignocellulosic alkaline extracts contain lignin and hemicelluloses in an oligomeric form, inorganic salts, acetic acid and phenolic monomers [8]. The separation of these compounds and their further valorization would provide added value for the biorefineries using mild alkaline pretreatment processes. The purification of some of these compounds has been studied with the use of several different methods including acid precipitation [9], ethanol precipitation [10], adsorption [11] and membrane filtration [12], but none of these methods has yet been adopted by industry.

Membrane filtration is of particular interest because of its low levels of chemical and energy consumption [13]. It can be performed on various streams of the lignocellulosic biorefinery: suspended solids can be retained by microfiltration (MF), or macromolecules, such as hemicelluloses and lignin, can be concentrated by ultrafiltration (UF) [14]. Monosaccharides, low molar mass lignin and phenolic monomers can be concentrated by nanofiltration (NF) and salts can be removed by reverse osmosis (RO) for water recycling.

Membrane filtration has been studied for the purification of hemicelluloses and lignin, mostly from the black liquors obtained in the strongly alkaline conditions used in the pulp and paper industry. Hemicelluloses retention of 69 to 81% have been achieved by the

ultrafiltration of black liquor on inorganic membranes [15], and hemicelluloses retention of 70% was obtained with a spiral wound membrane following the pulp steeping of viscose [16]. High hemi celluloses retention (over 90%) and intermediate lignin retention (30 50%) have been reported for pulp mill process water [17,18]. Some studies have reported lignin retention of up to 75% [19] or 80% [20] with total recovery in the permeate of black liquor salts. Compare to the severe alkaline conditions employed in the pulp and paper industry, the mild alkaline conditions studied in the second generation biorefinery produce a different extract, notably with longer hemicelluloses and lignin oligomers [21,22] or the absence of lignosulphonates and sodium hydrosulfide salts. Only a few studies have investigated the membrane filtration of lignocellulosic mild alkaline extracts [10,23]. However, these studies did not report retention values for all the components typically found in lignocellulosic mild alkaline extracts and flux beha vior was not discussed.

Retention of molecules and permeate flux (reflecting productivity) depend on the molecular weight cut off (MWCO) and type of mem brane, and the hydrodynamic conditions used. In studies on various hemicelluloses lignin strong alkaline extracts, the best MWCOs for high retention of hemicelluloses and lignin associated with low retention of smaller molecules were found to be in the range of 1 50 kDa [15,16,18,20,24]. Among the different membrane configurations, hollow fiber membranes present the best filtration area:volume ratio (m^2/m^3) [25]. Polysulfone (PS) is a common organic polymer used in hollow fiber membranes, with good mechanical, chemical and thermal stability [26]. Conversely, ceramic membranes have a longer life span than organic membranes [27], are more resistant to temperature and chemicals, and back washing is possible to remove fouling (pore blocking and cake formation). PS hollow fiber and ceramic tubular membranes are both suitable for use with alkaline extracts at pH values of up to 13.

In terms of hydrodynamic conditions, shear rate can be increased by raising the flow rate (or cross flow velocity or Reynolds number) and, thus, the energy consumption of the filtration unit. But the shear rate must be high enough to minimize the polarization layer and guarantee efficient cake removal, thereby maintaining a high permeate flux [28]. The transmembrane pressure (TMP) applied to the membrane must also be optimized. Increasing the TMP increases flux, thus increasing the productivity of the filtration unit, linearly at first, but the slope then becomes more shallow and a plateau known as the limiting flux is eventually reached, due to pore blocking, cake formation and/or in creases in the polarization layer. The inflection point of the curve after its linear region is known as the critical flux, and increasing the TMP above this point is generally not economically favorable [29]. Besides, increasing the TMP can also affect the retention of molecules in various ways, either reducing retention due to higher solution diffusion through the membrane below the critical flux, or increasing retention due to membrane fouling above the critical flux [18].

The aim of this work was to investigate in detail the influence of operating conditions (TMP, shear rate, temperature) on the performances of PS hollow fiber and ceramic tubular membranes for separating all the components of a model lignocellulosic mild alkaline extract. Sugarcane bagasse was used for this study, as it is one of the most produced and studied lignocellulosic biomasses for second gen eration biorefineries worldwide.

2. Materials and methods

2.1. Chemicals

Sodium hydroxide ($\geq 98.5\%$ purity) for the alkaline extraction, sulfuric acid 72% for NREL hydrolysis, 95% sulfuric acid and acetoni trile ($\geq 99.9\%$) for HPLC eluents were purchased from VWR, and cal cium carbonate (NREL protocol) was obtained from Merck. The fol lowing HPLC standards were purchased from Sigma Aldrich: D (+) cellobiose ($\geq 98\%$), D (+) glucose ($\geq 99.5\%$), D (+) galactose ($\geq 99\%$), L (+) arabinose ($\geq 99\%$), D (+) xylose ($\geq 99\%$), D (−) fructose ($\geq 99\%$), acetic acid ($\geq 99\%$), furfural (99%), 5 hydro xymethyl 2 furfuraldehyde (99%), gallic acid (97%), 4 hydroxybenzoic acid ($\geq 99\%$), caffeic acid ($\geq 98\%$), vanillic acid (97%), syringic acid ($\geq 95\%$), 4 hydroxybenzaldehyde (98%), vanillin (99%), *p* coumaric acid ($\geq 98\%$), syringaldehyde (99%), *trans* ferulic acid ($\geq 99\%$), sinapic acid ($\geq 98\%$), *trans* 3 hydroxycinnamic acid (99%).

2.2. Alkaline extraction

The alkaline extraction was carried out on 3 kg of SCB with 60 L of 1.5% NaOH (w/v) in a stainless steel lined vessel (De Dietrich), with a solid:liquid ratio of 1:20 (w/v) and a NaOH:SCB ratio of 1:3 (w/w), with continuous mechanical stirring (200 rpm) for 6 h at 60 °C. These are optimized conditions reported by Sun et al. (1995), for maximizing the recovery of hemicelluloses and lignin by the mild alkaline pre treatment of wheat straw [30]. The solid residue was removed from the alkaline extract using a top discharge vertical basket centrifuge (RC 50 PX R, Rousselet) equipped with a 5 μm polypropylene bag. This residue was rinsed with distilled water, dried at 50 °C for 48 h and ground by microfine grinder (IKA MF 10 basic) on a 1 mm sieve before analysis. The filtered SCB alkaline extract and the filtered solution used to rinse the solid residue were mixed, analyzed and used as the feed for the membrane filtration experiments (mixture referred to hereafter as the SCB alkaline extract).

2.3. Membrane filtration

2.3.1. Set up

Membrane filtration was carried out on the filtered SCB alkaline extract. Five new PS hollow fiber membranes (GE Healthcare) and two Kerasep ceramic tubular membranes (Novasep Process) were tested (Table 1). Reproducibility was assessed with another new 10 kDa PS hollow fiber membrane and a new 3 kDa PS hollow fiber membrane. The feed tank contained 5 L of water or filtered SCB alkaline extract.

Table 1
Characteristics of the membranes used for the filtration of sugarcane bagasse mild alkaline extract.

|	UFP-1-C-4 × 2M	UFP-5-E-4 × 2MA	UFP-10-E-4 × 2MA	UFP-30-E-4 × 2MA	UFP-50-E-4 × 2MA	K1335	K927
Module configuration	Hollow fiber	Hollow fiber	Hollow fiber	Hollow fiber	Hollow fiber	Tubular	Tubular
Membrane material	Polysulfone	Polysulfone	Polysulfone	Polysulfone	Polysulfone	ZrO_2/TiO_2	ZrO_2/TiO_2
Membrane area (cm^2)	1400	850	850	850	850	75	75
Number of fibers/channels	140	50	50	50	50	1	1
Channel inner diameter (mm)	0.5	1	1	1	1	6	6
Molecular weight cut-off (kDa)	1	5	10	30	50	5	15
Range of feed pH	2-13	2-13	2-13	2-13	2-13	0-14	0-14
Range of feed temperature (°C)	0-80	0-80	0-80	0-80	0-80	0-80	0-80
Range of feed pressure (bar)	0-3.1	0-3.1	0-3.1	0-3.1	0-3.1	0-6	0-6
Initial water flux (L/h/m²/bar) at 20 °C	21.3	40.7	47.5	76.3	113.2	38.1	57.0
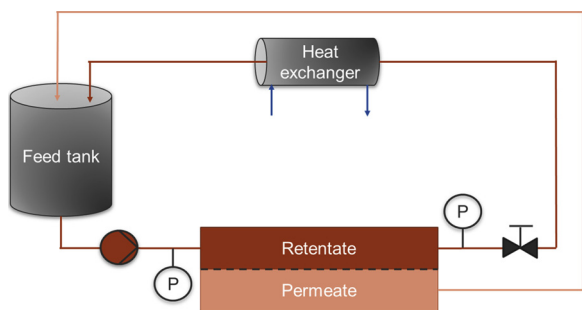
Fig. 1. Set-up of the filtration system used for the screening of membranes for the filtration of sugarcane bagasse mild alkaline extract.

The feed was circulated in the membrane with a gear pump (Johnson Pump, model 10/0005). Feed flow was measured with a flowmeter (Rosemount, Mexico). Permeate flux was assessed by collecting permeate over a given time period and weighing the sample collected. TMP was set with a valve on the retentate stream and checked with two manometers (Tecsis), one on either side of the membrane. The temperature was maintained at 20 °C during the experiments, with a monotube heat exchanger located in the retentate flow. When the effect of temperature was studied, the feed tank was heated to 40 °C with a hot plate (Heidolph). Experiments were run in recycling mode, with both the retentate and the permeate recirculated to the feed tank (Fig. 1).

Before each experiment, the new membrane (PS hollow fiber membranes were stored in glycerol), was washed several times with an ethanol/water solution (1:1, v/v), rinsed with water and the initial water flux (IWF) was measured at 20 °C and various TMP values. Water was drained from the installation and the SCB alkaline extract was loaded into the feed tank and recirculated at a TMP of 0.8 bar until the flux was stable over time (about 15 min) and a quasi stationary state was reached. Permeate flux was measured at different TMP values, from 0.8 to 2.8 bar, and different shear rates: 1966, 3408 and 4587 s^{-1} for ceramic tubular membranes (corresponding to cross flow velocities of 1.5, 2.6 and 3.4 m/s, respectively) and 3396, 6791 and 10,187 s^{-1} for PS hollow fiber membranes (corresponding to cross flow velocities of 0.4, 0.8 and 1.3 m/s, respectively). Nine permeate samples were collected for analysis at three different TMP values (0.8, 1.6 and 2.4 bar) and at the three shear rates tested. The feed volume was large enough relative to the total volume of permeates collected for analysis to assume that the composition of the SCB alkaline extract remained constant throughout each experiment. The final retentate was collected for analysis, to confirm that there had been no change in the composition of the SCB alkaline extract during the filtration process. At the end of the experiment, the SCB alkaline extract was drained and the membrane was washed several times with water.

2.3.2. Theoretical notions

The transmembrane pressure *TMP* is given by Eq. (1):

$$TMP = \frac{P_{inlet} + P_{outlet}}{2} - P_{permeate} \tag{1}$$

where P_{inlet} and P_{outlet} are the pressures (bar) at the inlet and the outlet of the membrane, and $P_{permeate}$ the pressure on the permeate stream. No back pressure was applied on the permeate side, so $P_{permeate} = 0$.

The shear rate γ (s^{-1}) is given by Eq. (2):

$$\gamma = \frac{4Q}{nr^3} \tag{2}$$

where Q is the flow rate (m^3/s), n is the number of channels or fibers and r is the radius (m) of a channel or fiber.

The retention R is given by Eq. (3):

$$R = 1 - \frac{C_P}{C_R} \tag{3}$$

where C_P and C_R are the solute concentrations (g/L) in the permeate and the retentate streams, respectively.

2.4. Analytical methods

The following analytical methods were applied to the initial SCB, the extract obtained following mild alkaline pretreatment (to determine its composition and extraction yields), and the various permeates obtained during the filtration experiments (to assess the retention of the various components of the SCB alkaline extract).

2.4.1. Dry solid and ash

Dry solid (DS) content was determined gravimetrically by heating at 103 °C for 12 h and ash content was determined at 500 °C for 12 h: 1 g was used for solid samples, 1 mL was used for alkaline extract and retentate samples, and 5 mL was used for permeate samples.

2.4.2. Carbohydrates and lignin

Based on Laboratory Analytical Procedure of the National Renewable Energy Laboratory [31], acid insoluble lignin (AIL) was quantified gravimetrically and acid soluble lignin (ASL) was determined spectrophotometrically, at a wavelength of 240 nm using an absorptivity constant of 25 L/g/cm. High performance liquid chromatography (HPLC) on a Rezex RPM Monosaccharide Pb^{+2} 300 x 7.8 mm column (Phenomenex), used in conjunction with a Rezex RPM Monosaccharide Pb^{+2} 50 x 7.8 mm guard column (Phenomenex) was performed to quantify the cellobiose, glucose, xylose, galactose, arabinose, mannose and fructose released by the acidic hydrolysis of cellulose, hemicelluloses or residual sucrose. Before injection, the samples were filtered on an ABW solid phase extraction (SPE) cartridge (Phenomenex) to remove salts and prevent interference with the sugar peaks. Isocratic conditions were used with Milli Q water at a flow rate of 0.6 mL/min; the injection volume was 20 µL, the column was maintained at 80 °C and the RI detector was maintained at 50 °C. For the alkaline extract and purified samples, HPLC on a Rezex RHM Monosaccharide H$^+$ 300 x 7.8 mm column (Phenomenex), used in conjunction with a Rezex RHM Monosaccharide H$^+$ 50 x 7.8 mm guard column (Phenomenex) was performed to quantify glucose, xylose, arabinose, acetic acid, furfural and hydroxymethylfurfural (HMF) [32]. The salts did not interfere with the sugar peaks on the RHM column, so, by contrast to the RPM column, no desalting of the samples was required before their injection. Isocratic conditions were applied, with 5 mmol/L H$_2$SO$_4$ at a flow rate of 0.6 mL/min; the injection volume was 50 µL, the column was maintained at 65 °C and the RI detector was maintained at 50 °C. The SCB alkaline extract and permeates collected were diluted by four fold with distilled water before the NREL protocol.

2.4.3. Monomeric sugars and hemicelluloses acetyl groups

Sulfuric acid was added to the alkaline extract to adjust its pH to 2, corresponding to the pH of the RHM column HPLC eluent. The extract was then analyzed on the RHM column without running the NREL protocol. The direct injection of pH adjusted samples onto the HPLC column made it possible to quantify monomeric sugars and free acetic acid, whereas the analysis of samples with the NREL protocol provided data for total sugars (monomeric and oligomeric forms) and acetic acid (free and bound to hemicelluloses).

2.4.4. Phenolic monomers

Twelve phenolic monomeric compounds potentially present in SCB alkaline extract [33,34]   gallic acid, 4 hydroxybenzoic acid, caffeic acid, vanillic acid (VA), syringic acid, 4 hydroxybenzaldehyde (4HBA), vanillin, *p* coumaric acid (*p* CA), syringaldehyde, ferulic acid (FA), sinapic acid and *trans* 3 hydroxycinnamic acid   were quantified by

HPLC on an OmniSpher 3 C18 100 × 4.6 column (Agilent Technolo gies). The gradient was as follows: 91% acidified water (1% acetic acid (v/v)) and 9% acetonitrile for 25 min, acetonitrile concentration in creasing from 9 to 90% over 5 min, then kept constant for 5 min, before decreasing back to 91% acidified water over 5 min, with column equilibration for 7 min between runs. The flow rate was 0.5 mL/min, the injection volume was 10 μL and the column temperature was maintained at 25 °C. The UV detector was set at 280 nm as it corre sponds to a maximum in the absorbance of phenolic monomers such as p CA and FA [35]. The concentrations used to plot the calibration curves ranged from 0 to 200 mg/L. Standards and process samples were diluted in acetonitrile:water at a ratio of 50:50 (v/v) before injection.

3. Results and discussion

3.1. Alkaline extraction

Glucan, xylan and arabinan were the only sugars detected in sig nificant amounts in the SCB. The SCB alkaline extract contained no monomeric sugars (glucose, xylose, arabinose and fructose); all the extracted sugars were under oligomeric form. No sugar degradation products (furfural and HMF) were detected and the acetate groups bound to hemicelluloses were completely hydrolyzed in the alkaline extract. Five of the 12 phenolic monomers tested — VA, 4HBA, vanillin, p CA, FA — were present in detectable amounts in the alkaline extract.

The composition of the SCB alkaline extract and the yields of the various components of SCB in this fraction are detailed in Table 2. The yields of dry solid and ash included the sodium hydroxide added in the process as detailed in Eqs. (4) and (5):

$$Yield_{DS} = \frac{m_{DS\,in\,alkaline\,extract}}{m_{dry\,SCB} + m_{NaOH}} \qquad (4)$$

Where $m_{dry\,SCB}$ is the mass of dry SCB introduced in the process, m_{NaOH} is the mass of sodium hydroxide used for the extraction and $m_{DS\,in\,alkaline\,extract}$ the mass of dry solid in the alkaline extract.

$$Yield_{ash} = \frac{m_{ash\,in\,alkaline\,extract}}{m_{ash\,in\,SCB} + m_{NaOH}} \qquad (5)$$

Where $m_{ash\,in\,SCB}$ is the mass of ash in the dry SCB introduced in the process, m_{NaOH} is the mass of sodium hydroxide used for the extraction and $m_{Ash\,in\,alkaline\,extract}$ is the mass of ash in the alkaline extract.

Only very small amounts of glucan (3%) were recovered in the extract. Xylan, arabinan, AIL and ASL were recovered at levels of 29,

Table 2
Initial sugarcane bagasse (SCB) composition, SCB mild alkaline extract com position and yield of the various components in the SCB mild alkaline extract.

Components	SCB Composition	Alkaline extract Composition	Yield
Dry solid	92.5	3.4	49
Ash	9.9	56.0	85
Glucan	35.9	1.4	3
Xylan	19.4	8.8	29
Arabinan	2.3	2.2	59
Acid-insoluble lignin	21.6	16.6	49
Acid-soluble lignin	5.5	8.2	96
Total lignin	27.1	24.6	58
Vanillic acid		traces	
4-hydroxybenzaldehyde		0.1	
Vanillin		0.1	
p-coumaric acid		3.3	
Ferulic acid		0.4	
Total phenolic monomers		3.9	

All these values were calculated as a percentage of dry solid. All analyses were run in duplicate.

59, 49 and 96%, respectively. Most of the salts (85%) were recovered in the alkaline extract, sodium hydroxide being the main one regarding the quantity introduced in the process compared to the ash content of SCB. Specific analyses for the identification of the inorganic salts of SCB were not carried out since these compounds constitute a minor fraction of SCB in terms of quantity and in terms of potential valorization.

The SCB alkaline extract used for all the membrane experiments consisted of six major pools of molecules: 19.4 g/L inorganic salts, 6.2 g/L AIL, 3.1 g/L ASL, 5.3 g/L oligomeric sugars (3.8 g/L xylan, 0.9 g/L arabinan, 0.6 g/L glucan), 1.5 g/L acetic acid and 1.3 g/L phe nolic monomers.

3.2. Membrane filtration

The effects of MWCO, TMP, shear rate, temperature and the nature of the membrane on permeate flux and the retention of the various compounds present in the SCB alkaline extract were evaluated in re cycling mode at quasi steady state. In most of the permeates analyzed, glucan and arabinan were barely detectable by HPLC. Xylan was, therefore, the only sugar oligomer studied in analyses of the permeate composition. Mass closure for each permeate composition was between 89 and 101%, so we can assume that the main compounds of the col lected permeates were analyzed.

3.2.1. Effect of time: quasi stationary state study

The effect of the experiment duration on the flux was investigated by recirculating the SCB mild alkaline extract at the lowest TMP (0.8 bar) and shear rate (3396 s^{-1}) (Fig. 2). On all three membranes tested, flux slowly decreased with a small change in magnitude, for instance, from 6 to 5 L/h/m^2 after 1 h for the 5 kDa PS hollow fiber membrane. Zeitoun et al. (2010) also observed a very small decrease in flux over time during the filtration of a wheat bran mild alkaline extract with a 30 kDa PS hollow fiber membrane from the same supplier but with a 0.5 mm fiber lumen [10].

3.2.2. Effect of MWCO
IWF increased with MWCO, from 21 to 113 l/h/m^2 for the PS hollow fiber membranes, confirming that, for a given type of mem brane, higher MWCO is associated with a higher water flux (Table 1). A similar trend was observed when SCB alkaline extract was recirculated at low TMP and low shear rate (Fig. 3A). At 0.8 bar and 3396 s^{-1}, the flux gradually increased with increasing MWCO for the PS hollow fiber membranes, from 3 L/h/m^2 for the 1 kDa membrane to 28 L/h/m^2 for the 50 kDa membrane. Only the 5 kDa membrane behaved differently with a flux similar to that for the 10 kDa membrane.

On PS hollow fiber membranes, at 0.8 bar and 3396 s^{-1}, the re tention of xylan, AIL and the ASL increased from 1 kDa to 10 kDa then decreased from 10 kDa to 50 kDa (Fig. 4). The highest retention rates were recorded for the 10 kDa PS hollow fiber membrane with values of 85%, 86% and 36% obtained for xylan, AIL and ASL, respectively. The evolution of the retention of ASL with MWCO was less marked than those of xylan and AIL, probably because phenolic monomers, which were accounted for in ASL (and also followed via HPLC on C18
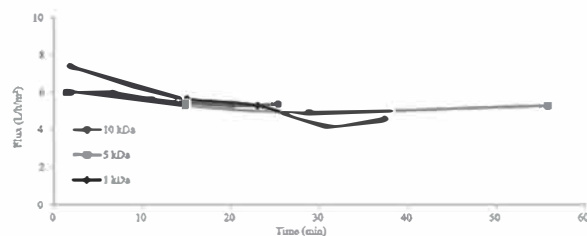

Fig. 2. Changes in permeate flux over time during the filtration of the su garcane bagasse mild alkaline extract at 0.8 bar and 3396 s^{-1} on three poly sulfone hollow fiber membranes.
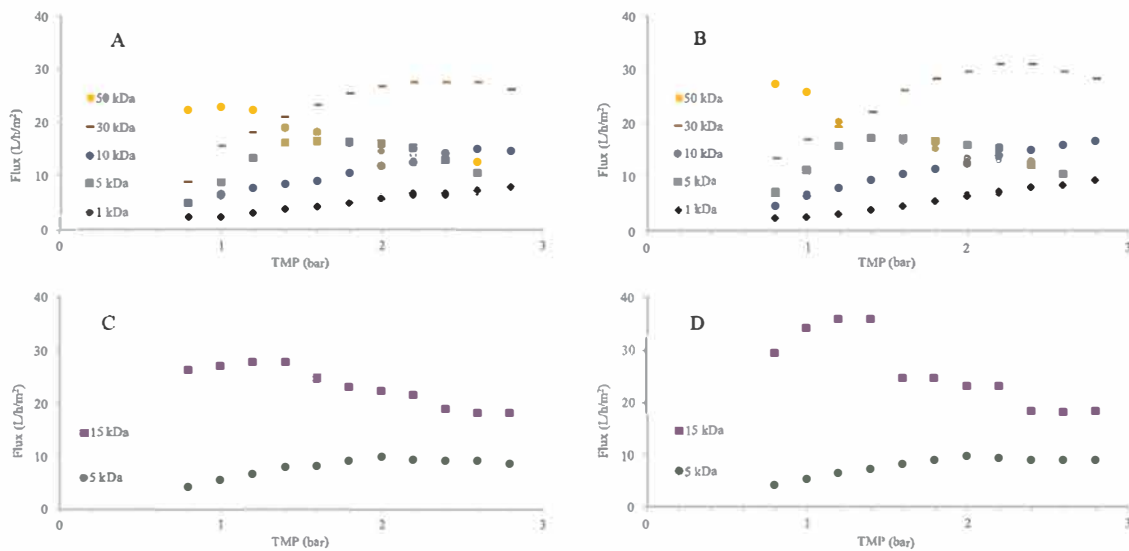
Fig. 3. Influence of the molecular weight cut-off, transmembrane pressure (TMP) and shear rate on the permeate flux during the filtration of sugarcane bagasse mild alkaline extract. (A) Polysulfone hollow fiber membranes with a shear rate of 3396 s^{-1}, (B) polysulfone hollow fiber membranes with a shear rate of 10,187 s^{-1}, (C) ceramic tubular membranes with a shear rate of 1966 s^{-1}, (D) ceramic tubular membranes with a shear rate of 3408 s^{-1}.

columns) passed through all the membranes (Fig. 5, only data for p CA are presented). The concentration of p CA in the various permeates ranged from 0.9 to 1.1 g/L, whereas that in the retentate/feed was 1.1 g/L. Similar trends were observed for vanillic acid, vanillin, 4HBA and FA. Likewise, acetic acid and ash concentrations did not differ significantly between the retentate and the various permeates, resulting in a retention close to 0%.

With the MWCO values tested, it was possible to separate xylan and AIL from phenolic monomers, acetic acid and ash, whereas ASL was moderately retained by the membranes. The retention of both xylan and AIL decreased with increasing MWCO (Fig. 4A&B), from 85 and 86% on the 10 kDa PS hollow fiber membrane to 64 and 46% on the 50 kDa PS hollow fiber membrane, respectively. Xylan and AIL from SCB alkaline extract could not be separated by filtration through PS hollow fiber membranes under the conditions tested.

3.2.3. Effect of TMP

On the 1 and 10 kDa PS hollow fiber membranes, permeate flux increased linearly with TMP (Fig. 3). On the 1 kDa PS hollow fiber membrane with a shear rate of 3396 s^{-1}, flux increased from 3 L/h/m² at 0.8 bar to 8 L/h/m² at 2.8 bar. With 10 kDa PS hollow fiber membranes at the same shear rate, flux displayed the same linear behavior but with a steeper slope, increasing from 5 L/h/m² at 0.8 bar to 15 L/h/m² at 2.8 bar. The linear increase in flux with TMP for these two membranes showed that the critical flux was not reached in the TMP range tested.

On the 5 kDa PS hollow fiber membrane, flux increased linearly with TMP up to 1.4 bar, at which the critical flux (16 L/h/m²) was reached. Critical flux and limiting flux merged into the same point on this membrane. For filtration with 30 kDa PS hollow fiber membrane, the critical flux (25 L/h/m²) was reached at 1.8 bar and the limiting flux (28 L/h/m²) at 2.2 bar. With the 50 kDa PS hollow fiber membrane, flux steadily decreased with increasing TMP. Rossi et al. (2008) also reported a decrease in flux with increasing TMP during the ultrafiltration of microalgae, probably due to polysaccharides retention, resulting in membrane fouling [28]. Here, the retentions of xylan or AIL were most likely accounted for the decrease in flux with increasing TMP for the PS hollow fiber membranes with higher MWCO. The limiting flux was reached within the range of TMPs used in the experiment, and the critical and limiting fluxes must therefore have occurred at TMP values below 0.8 bar. With the filtration system used, it was not possible to have a TMP lower than 0.8 bar at the shear rates tested, so it was not

possible to check the critical point on this membrane.

During this study, critical fluxes appeared at different TMP values for PS hollow fiber membranes differing only in terms of their MWCO values: under critical flux at 2.8 bar for 1 and 10 kDa membranes, critical flux at 1.4 bar for the 5 kDa membrane critical flux, at 1.8 bar for the 30 kDa membrane, and over critical flux and even limiting flux at 0.8 bar for the 50 kDa membrane. TMP critical flux decreased with increasing MWCO for all the membranes other than the 5 kDa PS hollow fiber membrane. In another study, Wu et al. (1999) observed a similar phenomenon when a colloidal silica suspension was filtered on poly ethersulfone flat sheet membranes with an MWCO of 50 and 100 kDa, and a PS flat sheet membrane with an MWCO of 0.2 μm [36].

An increase in TMP from 0.8 to 2.4 bar at a shear rate of 3396 s^{-1}, resulted in a slight increase in the xylan retention for all membranes tested, for instance, from 85 to 87% for the 10 kDa PS hollow fiber membrane and from 64 to 68% for the 50 kDa PS hollow fiber membrane (Fig. 4A). Persson and Jönsson (2010) observed that the retention of hemicelluloses decreased with increasing TMP below the critical flux, but increased with increasing TMP above the critical flux, during the filtration of pulp mill process water with 1 and 10 kDa polyvinylidene fluoride spiral wound membranes [18]. In this study, the retention of xylan increased with increasing TMP independently of critical flux.

Increase in TMP led to a moderate increase in AIL retention for all PS hollow fiber membranes except for the 50 kDa membrane, where AIL retention varied more significantly from 46% at 0.8 bar to 67% at 2.4 bar (Fig. 4B). The increase in ASL retention with TMP was clearly observed for all the PS hollow fiber membranes (Fig. 4C). Slightly higher retentions for small molecules (inorganic salts, acetic acid, phenolic monomers) were also observed, but their retentions did not exceeded 20%.

Overall, the change in retention with TMP was lower for PS hollow fiber membranes with smaller MWCOs (1, 5 and 10 kDa) than for those with larger MWCOs (30 and 50 kDa). As for the lowest TMP (0.8 bar), the 10 kDa PS hollow fiber membrane presented the highest retention for xylan (87%) and AIL (88%) at the highest TMP (2.4 bar).

3.2.4. Effect of shear rate

For the three shear rates tested, fluxes increased on all the PS hollow fiber membranes, but only to a limited extent (Fig. 3A&B, only the two extreme shear rates are presented). On the 1 kDa and 10 kDa PS hollow fiber membranes, a three fold increase in shear rate led to an increase of about 10% in flux on the TMP range tested. Behavior was different on
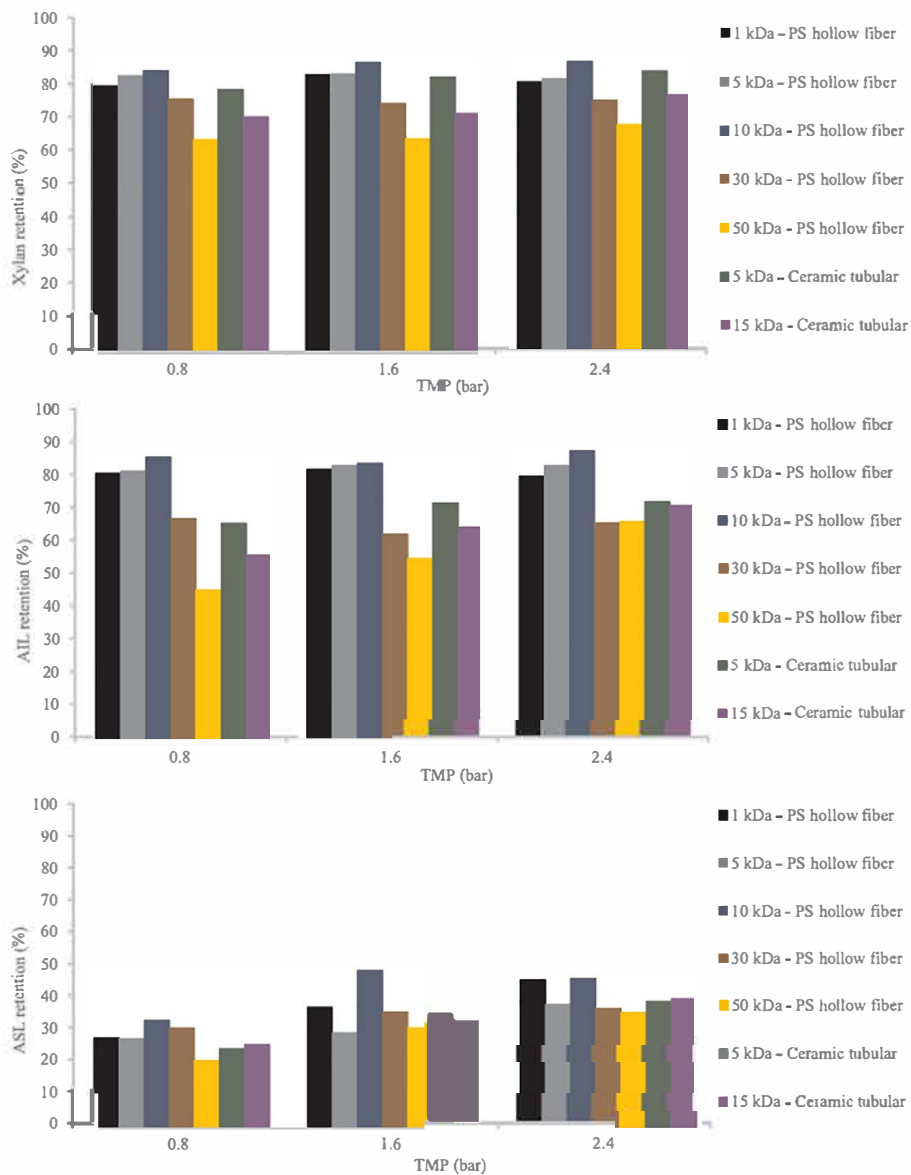
Fig. 4. Effect, during the filtration of sugarcane bagasse mild alkaline extract, of the molecular weight cut-off, the transmembrane pressure (TMP) and the nature of the membrane on the retentions of (A) xylan, (B) acid insoluble lignin (AIL) and (C) acid soluble lignin (ASL). Shear rate of 3396 s^{-1} for PS hollow fiber membranes and 3408 s^{-1} for ceramic tubular membranes.
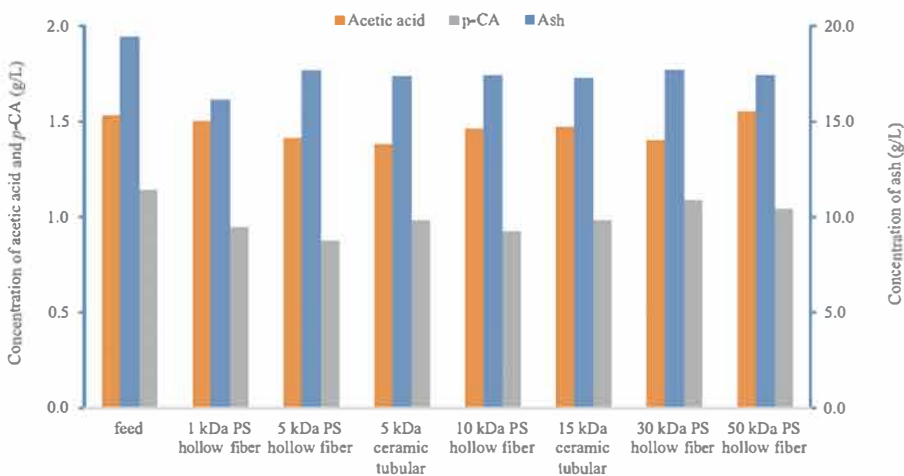

Fig. 5. Concentration of acetic acid, p-coumaric acid (p-CA) and ash in the feed and permeate of the seven membranes tested at 0.8 bar and shear rates of 3396 s^{-1} and 3408 s^{-1} for PS hollow fiber and ceramic membranes, respectively. The same trend was observed for vanillic acid, 4-hydroxybenzaldehyde, vanillin and ferulic acid but these molecules are not presented on this graph for the sake of clarity.
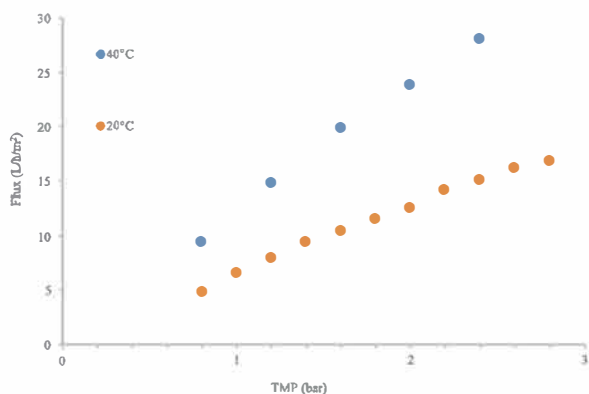
Fig. 6. Change in permeate flux evolution with transmembrane pressure (TMP) during the filtration of sugarcane bagasse mild alkaline extract on 10 kDa polysulfone hollow fiber membrane, with a shear rate of 10,187 s^{-1}, and temperatures of 20 °C and 40 °C.

the other PS hollow fiber membranes. On the 5 kDa PS hollow fiber membrane, the highest shear rate had a positive impact on flux but only below the critical point at 1.2 bar. On this membrane, for the three shear rates tested (Fig. 3A&B), the limiting flux was 17 L/h/m^2, and the flux began to decrease at 2 bar. On the 30 kDa PS hollow fiber membrane, the opposite effect was observed. Shear rate variations had no impact below the critical point, but above it, the lowest shear rate was associated with a lower flux. On the 50 kDa PS hollow fiber membrane, the highest shear rate increased the flux from 23 to 28 L/h/m^2 at the beginning of the TMP range, but at 2.6 bar, flux had fallen to 13 L/h/m^2 for all shear rates. Overall, a large increase in shear rate, from 3396 to 10,187 s^{-1}, triggered a limited increase in flux on all the PS hollow fiber membranes tested. A low shear rate may be sufficient to guarantee slow cake formation and/or minimization of polarization layer during the filtration. Shear rate had no significant effect on the retention of the molecules on any of the PS hollow fiber membranes.

3.2.5. Effect of temperature

Two temperatures (20 and 40 °C) were tested on the 10 kDa PS hollow fiber membrane at a shear rate of 10,187 s^{-1} (Fig. 6). At both temperatures, the retention of molecules passing through the membrane (inorganic salts, acetic acid, phenolic monomers) remained close to 0%. The increase in temperature (+ 20 °C) led to a doubling of the flux, for instance, from 5 to 10 L/h/m^2 at 0.8 bar and from 15 to 28 L/h/m^2 at 2.4 bar. In parallel, the retention of xylan and AIL decreased with increasing temperature, from 87 to 81% and from 88 to 79%, respectively. The decrease in the viscosity of the SCB alkaline extract and the dilation of the pores of the membrane may account for the increase in flux and the lower retention of large molecules at high temperature.

3.2.6. Effect of the nature of the membrane

Membranes made of different materials and with different configurations presented similar IWFs for the same MWCO. IWF was 38 L/h/m^2/bar for the 5 kDa ceramic tubular membrane and 41 L/h/m^2/bar for the 5 kDa PS hollow fiber membrane (Table 1). The IWF for the 15 kDa ceramic tubular membrane, 57 L/h/m^2/bar, was intermediate between the IWF values for the 10 and 30 kDa PS hollow fiber membranes (48 and 76 L/h/m^2/bar, respectively).

During filtration of the SCB alkaline extract, change in flux with TMP for the ceramic tubular membranes (Fig. 3C&D) was similar to that for PS hollow fiber membranes (Fig. 3A&B). The 5 kDa ceramic tubular membrane behaved similarly to the 5 kDa PS hollow fiber membrane, with a linear increase in flux with TMP up to a critical flux merging with the limiting flux, although the critical flux was lower (10 L/h/m^2) and was reached at a higher TMP (2.0 bar) for the 5 kDa ceramic

tubular membrane. The shear rates tested did not affect flux on this membrane. The 15 kDa ceramic tubular membrane had a similar flux versus TMP profile to the 50 kDa PS hollow fiber membrane. At the lowest shear rate (1966 s^{-1}) and TMP (0.8 bar), the critical flux had already been reached and the limiting flux (28 L/h/m^2) was reached at 1.4 bar. On this membrane, an increase in shear rate had a significant impact on the flux before the limiting flux, as limiting fluxes were 28, 36 and 48 L/h/m^2 for shear rates of 1966, 3408 and 4587 s^{-1}, respectively. For TMP values above that at which the limiting flux was achieved, shear rate had no influence on flux. Membranes of different composition and configuration yielded similar results in terms of the effects of MWCO, TMP and shear rate on flux.

The retention of xylan was similar on the 5 kDa ceramic tubular membrane and 5 kDa PS hollow fiber membrane, ranging from 79 to 84% at 0.8 and 2.4 bar, respectively (Fig. 4A). On the 15 kDa ceramic tubular membrane, xylan retention (71 77%) was lower and close to the values observed for the 30 kDa PS hollow fiber membrane (Fig. 4A). As for PS hollow fiber membranes, xylan retention on the ceramic tubular membranes increased significantly with MWCO and TMP, but was not influenced by shear rate.

AIL retention was significantly lower on the ceramic tubular membranes than on the PS hollow fiber membranes. For instance, on the 5 kDa ceramic tubular membrane, the AIL retention was between 66 and 73% depending on TMP, whereas retention values of 82 84% were obtained with the 5 kDa PS hollow fiber membrane. Ceramic materials are less hydrophobic than PS, potentially accounting for the lower retention of the hydrophobic AIL by ceramic membranes and the potential adsorption of AIL on the PS membranes. Inorganic salts, acetic acid and phenolic monomers were not retained on the ceramic tubular membranes either (Fig. 5).

As observed for PS hollow fiber membranes, an increase in TMP led to an increase in retentions for xylan, AIL and ASL on the ceramic tubular membranes, and shear rate had no significant effect on the retention of SCB alkaline extract components.

3.2.7. Repeatability study

Repeatability is often assessed on the same membrane, with successive filtration runs. The flux usually decrease over the filtration experiments, whereas the retention of the compounds gradually increase [16]. In this study, the repeatability test was run on a new 10 kDa PS hollow fiber membrane, to determine whether the selectivity and flux of the membrane presenting the best separation performances could be extrapolated to another new membrane. The two 10 kDa PS hollow fiber membranes presented similar linear flux behavior, with a slightly lower flux on the new membrane, with increases from 3 L/h/m^2 at 0.8 bar to 16 L/h/m^2 at 2.8 bar at 10,187 s^{-1} (Fig. 7). Retention of the various compounds were also similar in the different conditions tested, with values of 91% for xylan and 82% for AIL at 2.8 bar on the second membrane tested (Fig. 7).

Concerning the different flux versus TMP profiles of the 5 kDa PS hollow fiber membrane, and the 1 and 10 kDa PS hollow fiber membranes, changes in flux with TMP were assessed on a new 3 kDa PS hollow fiber membrane from the same supplier. The same flux behavior as reported for the 5 kDa membrane was observed, with merging critical and limiting fluxes (18 L/h/m^2 at low shear rate and 19 L/h/m^2 at high shear rate) reached at 1.4 bar, regardless of shear rate (Fig. 7). The difference in flux behavior on these two membranes relative to the 1 and 10 kDa PS hollow fiber membranes showed that the results obtained for a given MWCO cannot be extrapolated to other membranes of the same type with different MWCO values for the filtration of SCB alkaline extract.

4. Conclusion

During the ultrafiltration of SCB alkaline extract, xylan and AIL were retained in the retentate to different extents, depending on the
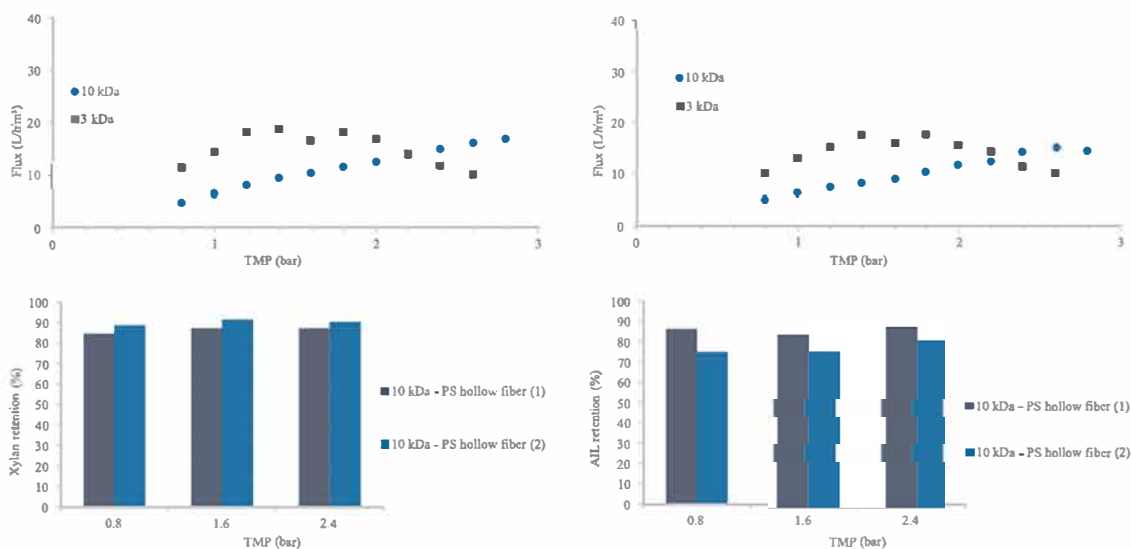
Fig. 7. Repeatability study on new 3 and 10 kDa polysulfone hollow fiber membranes for the filtration of sugarcane bagasse mild alkaline extract. (A) Flux vs transmembrane pressure (TMP) profile at a shear rate of 3396 s^{-1}, (B) flux vs. TMP profile at a shear rate of 10,187 s^{-1}, (C) xylan retention on the two new 10 kDa polysulfone (PS) hollow fiber membranes, (D) acid-insoluble lignin (AIL) retention on the two new 10kDa polysulfone hollow fiber membranes.

membrane used, whereas almost no retention of salts, acetic acid and phenolic monomers (vanillic acid, 4HBA, vanillin, p CA, FA) was observed. Sugar oligomers and lignin oligomers from SCB mild alkaline extract cannot be separated by membrane filtration. The retentions of these large molecules were not completely inversely proportional to the MWCO of PS hollow fiber membranes. A maximum retention close to 90% was obtained for xylan and AIL with 10 kDa PS hollow fiber membrane. At the maximum TMP tested (2.8 bar), the critical flux had not yet been reached, and a permeate flux of 16 L/h/m^2 was achieved at 20 °C.

Filtration in concentration mode of the sugars and lignin oligomers on this membrane should lead to high recoveries of these compounds and to the removal of inorganic salts, acetic acid, phenolic monomers and ASL to a lesser extent. The concentration of the retained compounds in the retentate would probably lead to higher retention due to the build up of a polarization layer and a cake at the surface of the membrane. Membrane filtration presents the advantage of not only separating molecules, but also concentrating the retentate stream which is particularly useful if the next step in the purification process requires a concentrated feed, as is the cases for chromatography or precipitation. By performing ultrafiltration before selective precipitation, it would be possible to obtain pure hemicelluloses or lignin fractions (free of salts, phenolic monomers, acetic acid), a key advantage given that the main concern raised about selective precipitation on lignocellulosic alkaline extracts is the low purity of the supernatant and the precipitate. Diafiltration could be investigated as a way of eliminating additional inorganic salts, acetic acid and phenolic monomers, if a higher purity of retained compounds is required.

Acknowledgments

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