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Organosolv pretreatment for cellulose recovery from sawdust for its ulterior use in membrane synthesis and operation

Lourdes Ballinas-Casarrubias[a,*], Tania Saucedo-Acosta[a], Karen MacDonald-Pizaña[b], Karla Ruiz-Cuilty[b], Guadalupe Virginia Nevárez-Moorillón[a], Néstor Gutierréz-Méndez[a], Carles Torras-Font[c], David Chávez-Flores[a], Guillermo González-Sánchez[b]

[a]*Facultad de Ciencias Químicas, Universidad Autónoma de Chihuahua, Nuevo Campus s/n, Chihuahua, Chih., México, emails: mballinas@uach.mx, lourdes.ballinas@gmail.com (L. Ballinas-Casarrubias), tania_saac@yahoo.com.mx (T. Saucedo-Acosta), vnevare@uach.mx (G.V. Nevárez-Moorillón), ngutierrez@uach.mx (N. Gutierréz-Méndez), dchavez@uach.mx (D. Chávez-Flores)*

[b]*Centro de Investigación de Materiales Avanzados (CIMAV), Miguel de Cervantes 120 Compl. Ind. Chihuahua, CP 31109 Chihuahua, Chih., México, emails: karen.macdonald@cimav.edu.mx (K. MacDonald-Pizaña), karla.ruiz@cimav.edu.mx (K. Ruiz-Cuilt), guillermo.gonzalez@cimav.edu.mx (G. González-Sánchez)*

[c]*Catalonia Institute for Energy Research, IREC, Marcel lí Domingo 2, 43007 Tarragona, Spain, email: ctorras@irec.cat*

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ABSTRACT

Pinus sp. sawdust was pretreated by the ethanosolv process using $AlCl_3$, $FeCl_3$, and H_2SO_4 as catalysts in order to be compared with the methods that are traditionally used to recover cellulose. The ethanosolv process was carried out using different catalysts, different processing time (30, 45, and 60 min), and different temperatures (170,180°C) according to a $3 \times 3 \times 2$ full-factorial experimental design. For cellulose recovery, lower times and temperatures produced the highest yields (up to 58% dry based). Acetylation of the lignocellulosic material obtained was done using acetic anhydride and sulfuric acid. The esterification degree (%ED) of the material was measured by saponification and back-titration of the residual NaOH. Values of %ED ranged from 25.62 ± 1.21 to 39.62 ± 1.75 with no significant differences among treatments. The acetylated cellulose was recovered with methylene chloride and membranes were produced by the EP method. In order to characterize the films obtained, FTIR, SEM, and Rheometry analysis were performed. Infrared spectra revealed acetylation. Microscopy evidenced dense materials for all conditions, and membrane thickness was calculated. Membranes with the highest Young modulus (YM = 297.2 Pa) were produced with the chemically pulped cellulose. The membranes obtained are useful for micro- and ultrafiltration processes; a strong correlation in rejection was related with lignin content of the raw acetylated material. Water fluxes ranged from 10.45 to 51.56 L h^{-1} m^{-2} bar^{-1} and calcium rejection values were up to 89.75%.

Keywords: Membranes from biomass; Sawdust; Organosolv pretreatment

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*Corresponding author.

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1. Introduction

Membrane technology is one of the main processes used for water treatment. In the north part of Mexico, water scarcity originated by long drought periods in a semiarid and arid environment has produced serious disorders in water supply for human consumption. Due to the geological composition of underground water deposits, mineral lixiviation has promoted the presence of highly toxic metals, with higher concentration than the allowed maximum limits. In this regard, governmental organizations have encouraged the use of advanced technologies for water purification. Actually, there are around 365 osmosis plants in the state of Chihuahua, Mexico. The main problem related with this technological implementation is membrane replacement; membrane production using economic materials could be a good alternative for their operation. Recently, our results on membrane production using cellulose chemical derivatives have been reported [1–6]. These membranes are used in combination with activated carbon or chemically modified lignin and are even superior compared with the commercial acetate cellulose membranes, because of their mechanical and biological properties [7].

Agroindustrial and forestry activities annually produce large quantities of wastes, causing an alarming environmental impact [8]. Specifically in Mexico, wood processing in sawmills along the country generate constantly huge amounts of this residue. During 2011, 3.9 millions of cubic meters of wood were destined to production, and generated 100 tons of waste. Chihuahua is the largest producer of *Pinus* sp. in the country with an annual production of 1,003,505 roll cubic meters [9]. Generally, subproducts are used directly as fuel or to manufacture agglomerated materials, but this usage is not enough to overcome the problems of its disposition [10].

Sawdust, as a lignocellulosic feedstock, contains three main biopolymers: cellulose, hemicellulose, and lignin. Due to their chemical composition based on sugars, they could be used for the production of a number of value-added products [8]. One possible application is membrane synthesis, similar to those reported for other biomass materials, like sugarcane bagasse [3,11], mango seed, and newspaper [12]. In this work, acetylated cellulose membranes have been obtained from *Pinus* sp. sawdust previously pretreated to obtain the highest cellulose yield.

Many processing alternatives are being studied to efficiently recover biomass polymers (Table 1) [13,14]. The main purpose of pretreatment is to remove as much hemicellulose and lignin as possible, while simultaneously keeping enough cellulose intact [15,16]. Fractions with a high yield of cellulose depend on the pretreatment method [17]. Pretreatment still remains the most expensive and time-consuming step in biomass conversion; furthermore, it is very difficult to generalize the process conditions even for a similar type of biomass due to the broad variability of the raw material composition, nature, variety of species, conditions of production, and even between batches [18,19]. Cellulose is currently separated from lignocellulosic materials using nonenvironmental friendly processes, such as kraft, sulfite, and soda treatments, with consequent generation of toxic wastes [20]. In the last few years, a new philosophy has been developed due to the growing restrictions in the environmental laws, based on the sustainable processing of biomass into value-added products [21].

The ethanol organosolv process is among the green-pretreatment strategies currently being studied for the conversion of lignocellulosic biomass feedstocks [22–24]. It was originally developed as the Alcell® pulping process for hardwoods [25,26]. Recent studies focused on the evaluation and optimization of this pretreatment for the delignification of softwood, hardwood, and agricultural residues have shown that the organosolv pretreatment yields substrates with good cellulose recovery and low-lignin content [27–31].

In the ethanosolv process, an organic or aqueous organic solvent mixture with inorganic acid catalysts (HCl, H_2SO_4) is used to break the lignin and hemicellulose bonds [32]. Ethanosolv is a more convenient method than other pretreatments, because it is safer than any other organosolv pretreatment. Ethanol is less toxic than the other solvents, which can also be recovered easily through distillation; however, acid-catalyzed treatments have several limitations [30,31,33]. First, the acid itself is not an environmental-friendly reagent, and the discharge could lead to environmental pollution; second, its corrosiveness requires expensive construction materials, which increase the cost of the pretreatment [34].

Inorganic salts were studied as a substitute in order to avoid these side effects, being by themselves less corrosive than acids and they can also be recycled [27,35]. The pretreatment process is more economically viable if inorganic salts in aqueous solution can be directly used in the pretreatment of the lignocellulosic biomass; this process would avoid further overliming in order to neutralize the hydrolyzate [36,37].

Several studies have reported that the addition of inorganic salts can increase the hydrolysis rate of hemicellulose and cellulose in the biomass during dilute acid pretreatment. The inorganic salt has a strong catalytic effect on the hydrolysis process, since

Table 1
Summary of the various processes used for the pretreatment of lignocellulosic biomass

Pretreatment	Advantage	Limitations
Steam explosion [55]	Causes degradation of hemicellulose and lignin transformation; effective cost	Incomplete disruption of lignin-carbohydrate matrix
Fiber explosion with aqueous ammonia [56]	Increase the accessibility area, removes a large amount of lignin and hemicellulose, does not produce inhibitors for subsequent processes	It is not efficient with biomass with a high content of lignin
Explosion with CO_2 [50]	Increases the accessibility area, does not produce inhibitors for subsequent processes	Unchanged lignin or hemicellulose
Ozonólisis [57]	Reduces the lignin content; do not produce toxic waste	Large amounts of ozone are required, it is an expensive process
Biological [58]	Degrades lignin and hemicellulose; low energy requirement	The hydrolysis speed is very low
Organosolv [36]	Hydrolyzed lignin and hemicelluloses	Solvents need to be drained from the reactor, evaporated, condensed, and recycled: high cost

cellulose recovery can be as high as 90%, and after pretreatment, 88.5% of the added salt could be removed through a washing/filtration process, which indicated that it had no effect on the subsequent processes [36].

In this work, we report a comparison of diverse catalysts in organosolv pretreatment, contrasted to traditional methods for cellulose recovery from sawdust. All cellulose obtained was used for ulterior esterification and membrane production. Membranes were characterized by FTIR, SEM, and Rheometry in a cation-permeation process.

2. Methodology

2.1. Organosolv pretreatment and characterization

2.1.1. Organosolv pretreatment

The ethanosolv process was carried out using different catalysts (0.1 M for $FeCl_3$ or $AlCl_3$ or 1% v/v for H_2SO_4), different processing time (30, 45, 60 min), and different temperatures (170 and180˚C) according to a $3 \times 3 \times 2$ full-factorial experimental design. To determine if there were significant differences among the treatments, a statistical analysis was performed by ANOVA. Tukey's analysis was performed by Minitab software version 17 (Minitab, 2014). Table 2 shows the experimental conditions for ethanosolv pretreatment. Two grams of sawdust (2.38 mm mean particle size) were weighted and mixed with 10 mL of an aqueous ethanol solution of 50% (v/v) corresponding to a 5:1 ratio (v/w). The mixture was heated to the desired temperature in an oil bath at various reaction time and catalysts.

This procedure was carried out in 10 reactors (316 SS batch reactor with an internal volume of 20 mL) for each reaction condition. The reactors were adapted using 1´´ double ferrule tube fitting A-lock® with two plugs A-lock®. They were heated by immersion into an oil bath, three at the same time. A mechanical shaker mounted in oil bath's cover held each reactor having 30 cycles per minute inside the oil. Reactors held by pliers were manually stirred every 5 min. Time required to reach the reaction temperature was monitored using one testing batch reactor with one plug with a connection to insert a thermocouple. This time was 45–60 s depending on the final temperature. Zero time to start measuring total reaction time was determined under this criterion. The reactor was cooled immediately when the final time was reached by immersion in an isothermal ice-water bath at 5˚C to cool down the reactors to 80˚C in 45–60 s.

The solid residue and liquor obtained from the pretreatment were separated by filtration with nylon cloth. The solid fraction was further washed with an aqueous solution of ethanol 50% (v/v) preheated at 60˚C, and it was stored until analysis of lignin and carbohydrates. The treated biomass was dried at 45˚ for 24 h and refrigerated for further acetylation.

The liquid fraction from the filtration was mixed with three volumes of water to precipitate the dissolved lignin (organosolv lignin ethanol soluble, EOL). Lignin was filtered and the filtrate (water soluble fraction) was analyzed for the determination of soluble lignin (by UV spectrophotometry, Section 2.1.6).

2.1.2. Chemical pulping

In order to liberate the cellulose from the rest of the sawdust components, the aqueous and organic sawdust extractives were subtracted previously

Table 2
Experimental conditions for organosolv process

Pretreatment	
Ethanol concentration (% v/v)	50
Temperature (˚C)	170,180
Reaction time (min)	30, 45, 60
Catalyst employed	$FeCl_3$,$AlCl_3$, H_2SO_4
Catalyst concentration	0.1 M ($FeCl_3$,$AlCl_3$) and 1% v/v (H_2SO_4)

according to the standardized methods ASTM D1110-84 and ASTM D1107-84, respectively. Afterwards, the biomass was subjected to acid hydrolysis as follow: 20 g of sawdust was put in contact with 10 mL H_2SO_4 in autoclave for 15 min. The obtained material was treated with NaOH at 1.5% in order to remove most of the lignin. The pulp was rinsed to neutral pH and then it was dried at room temperature.

2.1.3. Bleaching

The pulp (from Section 2.1.2) was bleached using sodium hypochlorite (1.25% v/v). At this stage, the remaining hemicelluloses were broken, and the xylan and lignin were released. The pulp was rinsed until neutral pH and it was dried at room temperature.

2.1.4. DRX analysis

Each sample was analyzed using an X-ray powder diffractometer model X'Pert MPD Phillips, with Cu Kα monochromatic radiation and θ–2θ geometry. Powder XRD patterns were obtained from 10 to 80˚ 2θ angle range in step-scanning mode with a step length of 0.0204˚ and a step-counting time of 0.725 s.

2.1.5. Determination of carbohydrates and organic acids for HPLC

Two grams of the sample were transferred into a 100 mL beaker. Then, 10 mL of H_2SO_4 (72%) was poured under vigorous stirring in a thermostated bath (45˚C) for 7 min. The reaction was stopped by adding 50 mL of distilled water. Immediately, the sample was quantitatively transferred to a 500 mL Erlenmeyer, increasing the volume to 275 mL water. For complete hydrolysis of the remaining oligomers, the Erlenmeyer was closed with aluminum foil and autoclaved for 15 min at 1.05 atm. After decompression, the flask was removed from the autoclave and cooled to room temperature. The percentages of cellobiose, glucose, xylose, arabinose, and acetic acid in the hydrolyzate were analyzed by high-performance liquid chromatography (HPLC). A small sample of the solution was filtered with a Sep Pak C18 filter and analyzed by HPLC (Agilent 1100) using a refractive index detector and a stationary column Aminex HPX 87H (300 x 7.8 mm, BIO-RAD). The mobile phase used was H_2SO_4 0.005 mol L^{-1} with flow of 0.6 mL min^{-1} at 45˚C.

The mean areas of the chromatograms for cellobiose, glucose, xylose, arabinose, and acetic acid became equivalent of cellulose, hemicellulose, and acetyl groups, respectively. Masses were divided by the dry weight of the initial material and then multiplied by the factor of hydrolysis. Conversion factors for glucose, cellobiose, and cellulose were 0.90 and 0.95, respectively. Similarly, xylose and arabinose were converted to hemicellulose using the factor 0.88. The conversion factor of acetic acid to acetyl group was 0.72.

The concentrations of the compounds were determined from calibration curves plotted for each component.

2.1.6. Determination of total lignin

To determine soluble and insoluble lignin, samples from each fraction were hydrolyzed.

The hydrolyzate material was separated from the solids by filtration. The hydrolyzate was collected in 500 mL volumetric flask and the solid content on the filter paper was washed with 50 mL portions of distilled water until reaching the volume of the flask, which is stored for later analysis. The lignin retained in the filter paper was washed with distilled water until reaching the elimination of sulfates (approximately 1.5 L) and dried in oven at 105˚C till constant weight. To determine the soluble lignin, 5 mL part of the hydrolyzate obtained was basified with 1 mL of 6 mol L^{-1} NaOH until pH 12 and then was diluted in a 50 mL volumetric flask. This solution was analyzed by UV spectroscopy, determining the absorbance of the solution at 280 nm wavelength using NaOH as a reference.

2.1.7. *Determination of total ashes*

Ashes were determined gravimetrically, using a controlled analytical balance with known moisture. They were calcined in a muffle furnace at 800˚C for 2 h. After calcination, the crucible was cooled into a desiccator and the mass of ash was determined.

2.2. *Membrane production*

2.2.1. *Acetylation*

Acetylation was made to the biomass already treated, where most of the hemicellulose and a fraction of lignin have been removed. Therefore, cellulose is more available for modification. To acetylate the cellulose, treated biomass (100 g) was kept in a water bath at 38˚C for 1 h with glacial acetic acid (240 g) at constant agitation. Then, more acetic acid (480 g) and a small amount of sulfuric acid (0.88 g) were added. The temperature was maintained for 45 min. Then, the mixture was cooled to 18˚C and more acetic anhydride was added (270 g), maintaining the temperature between 32 and 35˚C for 1.5 h. Afterwards, a solution of water and acetic acid (1:2) was gradually added, for one hour under stirring at 38˚C. The resultant acetylated biomass was finally filtered and dried at room temperature.

2.2.2. *Membranes by evaporation–precipitation (EP)*

The acetylated biomass was dissolved in methylene chloride. The flask was kept at controlled temperature (25˚C) in a shaker for a period of 24 h. Afterwards, the flask content was filtered to subsequently form the membrane. The obtained filtrate (25 mL) was poured into petri dishes (9 cm diameter). The solvent was evaporated in a temperature and relative humidity (RH)-controlled chamber (Shellab). The temperature was kept constant at 35˚C, with a RH = 20%. The approximate formation time was 4 h.

2.2.3. *Ester content*

To determine the ester content, a saponification reaction between the membrane and NaOH was performed. The membrane was cut into small pieces (0.1 g) and put in contact with 4 mL of ethanol (Baker, 95%). The flask was heated for 30 min at 55˚C. After this time, a volume of 2.5 mL of NaOH 0.5 N was added and maintained at 55˚C for 15 min, under stirring. The mixture was allowed to react for three days. Then, a back titration with 0.5 N HCl (normalized) was done. The ester content (esterification degree, ED) was calculated by the following equation:

$$\%ED = [(A - B) * N_B - (C - D) * N_A] * \frac{M}{10 * P}$$

where A and B are the mL of NaOH added to the acetylated sample and the blank, respectively. C and D are the mL of HCl used to neutralize the acetylated sample and the blank, respectively. N_A and N_B are the normal concentrations of HCl and NaOH. P is the sample weight and M is the molar mass of the acyl group added to the cellulose [38].

2.2.4. *Fourier transformed infrared spectroscopy (FTIR)*

FTIR was made with an attenuated total reflectance (FTIR/ATR, Perkin Elmer, Spectrum GX; USA) equipment operating at 4 cm^{-1} resolution. The mirror velocity was 0.08 cm^{-1} and four interferograms were co-added before Fourier transformation spectra were collected from 650 to 4,000 cm^{-1}. Analysis of treated biomass and membranes were performed for comparison.

2.2.5. *Scanning electron microscopy*

Membrane samples were placed in an aluminum plate and coated with a thin layer of gold in a covering system (Denton Desk-II Gatan). The scanning electron microscope (JEOL JSM-5800LV, Japan) was used at an accelerating voltage of 10–20 kV. SEM micrographs were taken at 15 kV in top, bottom, and edge views at 200×.

2.2.6. *Permeability tests*

The membranes were tested in a continuous flow cell (Sepa Osmonics) with a filtration area of 0.0009 m^2. Operating pressure was recorded and the flux was calculated with water as feed. Rejection was made with a synthetic solution of 8.75 ppm calcium and 250 ppm of sodium as feed. Ions were analyzed by ICP-MS.

2.2.7. *Rheometry*

A rheometer (AR 2000 ex, TA Instrument Ltd.) equipped with a parallel steel plate of 40 cm diameter was used for mechanical analysis. Membranes were cut in discs of 4 cm diameter, previously hydrated. Strain sweep step were performed with the following parameters: strain 0.05–5.0%, oscillation frequency 1 Hz, and temperature 20˚C. Rheology advantge data analysis program was used to process data obtained of strain–stress tests. Young moduli were calculated from the linear relationship between shear stress and strain

3. Results and discussion

3.1. Organosolv pretreatment and characterization

3.1.1. Characterization of Pinus *sp.* sawdust

The composition of sawdust was determined on a dry basis. The results were: cellulose 32.51 ± 4.7; hemicellulose 16.27 ± 3.8; lignin 39.59 ± 0.4; others 10.53 ± 0.36 (Table 3). There is a wide variation in the amount of cellulose in wood, which depends on the source mainly. For soft wood (such as *Pinus* sp.) it was found that cellulose content ranges from 40 to 50% [39,40].

In our study, the amount of cellulose and lignin are lower than the ones reported previously, mainly because the material came mostly from pine bark. In regard to the large fraction which is known as extractives, it depends on the type of wood, tree age, and environmental conditions under which the plant grew [41].

3.1.2. Cellulose released by traditional methods

Cellulose was released by the traditional methods, chemical pulping (*P*) and bleaching (*B*), in order to be contrasted with the organosolv treatment. Cellulose, hemicellulose and lignin content of the biomass treated are shown in Fig. 1. When *P* and *B* are used, hemicellulose decreased approximately to 50%. This decrement is due to the use of NaClO, which solubilizes these compounds oxidizing the lignin that is covalently linked.

Kumar et al. mentioned that hydrolysis with low acid concentrations (2–5%) at high temperature (160–130˚C) hydrolyzes hemicellulose, maintaining cellulose structure almost unaltered [42]. If acid concentration increases (10–30%), glucose will be produced at low temperature (50˚C), hydrolyzing the cellulose initially found. More than 50% of the initial lignin content and more than 95% of the initial xylan were removed.

3.1.3. Organosolv pretreatment

The organosolv process has been investigated to extract lignin from pulp. In this process, an organic or aqueous organic solvent is mixed with a catalyst (usually an inorganic acid such as HCl or H_2SO_4) to break the bonds of the lignin and hemicellulose [36]. Other catalysts used for ethanosolv are oxalic, salicylic, and acetylsalicylic acid. The goal of the pretreatment is to remove the maximum amount of lignin and hemicellulose as possible, while maintaining the cellulose intact.

Abeywickrama et al. found that the optimal conditions, from the cellulose and lignin recovery point of view starting from biomass, were in the temperature range from 150 to 190˚C [43]. Sulfuric concentration was between 0.5 and 1.2%, and reaction time was around 60 min; among these parameters, temperature and acid concentration were the ones with more significant effect. In ethanosolv pretreatment, cellulose rich pulps were obtained with very low hemicellulose content.

When dissolved in water, a small cation with high charge (such as Al^{3+} and Fe^{3+}) is generated, i.e. a Lewis acid. As a result of coordination of the cation with water molecules, a proton is released. Protons released promote the breakup of the ether and ester bonds that join lignin with holocellulose. Several authors have tried to explain the type of covalent bonds between lignin and carbohydrates; however, results are not conclusive [44].

Table 3
Comparison of lignocellulosic material compositions (Results expressed on dry weight)

References	Raw material	Cellulose	Hemicellulose	Lignin	Ashes
[59]	*P. radiate*	45.3	22.2	26.8	0.2
[60]	Rice straw	32–37	19–27	5–24	12.4
[61]	Wheat straw	35–45	20–30	8–15	10.1
[62]	Waste of corn	42.6	21.3	8.2	4.3
[36]	Barley straw	47	21	22	–
[63]	Sugar cane bagasse	45.5	27	21.1	2.2
This work	Sawdust *Pinus* sp.	32.51	39.69	16.27	1.23

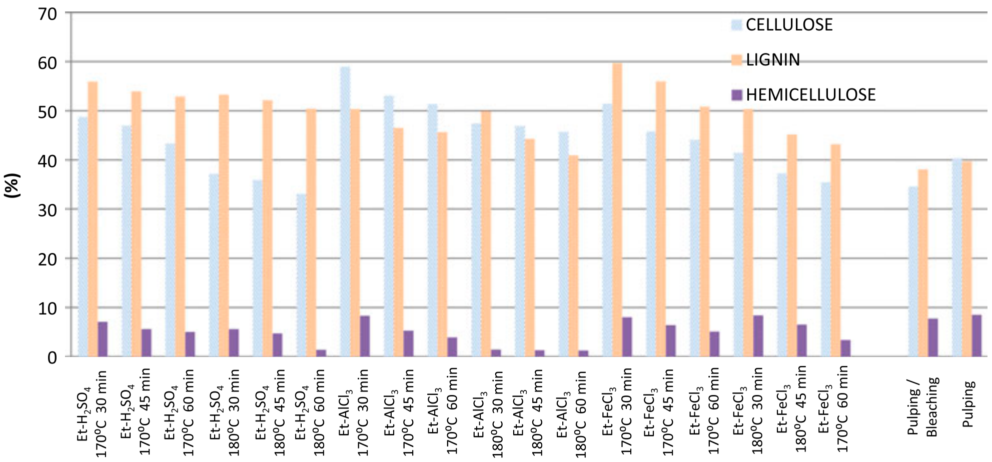

Fig. 1. Biomass composition after pretreatments. Cellulose, hemicellulose, and lignin in the solid fraction.

Cellulose yield for each organosolv pretreatment is illustrated in Fig. 2. The amount of cellulose that remains on the solid substrate relative to the original amount of cellulose is almost 100% for the treatments at 170˚C, where $AlCl_3$ or $FeCl_3$ are used as catalysts. Thus, the inorganic salts leave practically intact the cellulose in the solid biomass. Meanwhile, when H_2SO_4 is used, yields decrease to 80%. This is because H_2SO_4 has greater affinity to catalyze the degradation of cellulose for the production of inhibitors than the salts [45]. At 180˚C, there is a notable decrease in the cellulose, with yields lower than 80%. $AlCl_3$ is the catalyst with the highest performance of cellulose (76%) at 30 min reaction time. This yield affects the final cellulose balance in the solid fraction.

Generally, the recovery of cellulose in pretreated sawdust is higher at low temperatures and short reaction times for the three catalysts. This is because the cellulose is degraded to products such as hydroxymethylfurfural and furfural. This production increases as the temperature also increases (Arrhenius kinetic effect) and it is bigger for longer residence times in the reactor. The chemical composition of the products obtained in the liquor is really complex, where condensation compounds from the fractioned lignin are evolved [46].

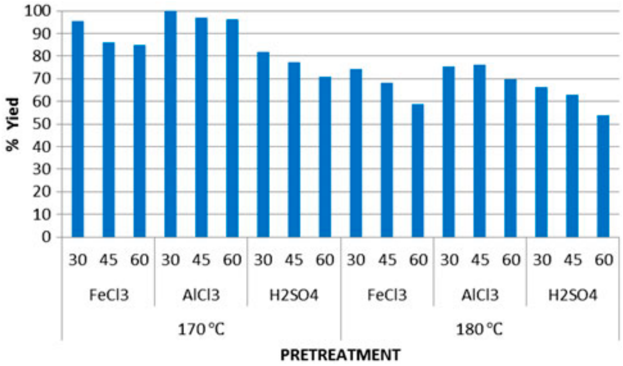

Fig. 2. Cellulose yield according for each organosolv pretreatment.

Fig. 1 shows the concentration of cellulose, lignin, and hemicellulose obtained in the pine sawdust pretreated at different temperatures (170 and 180˚C), different reaction time (30, 45, and 60 min), and catalysts employed ($FeCl_3$, $AlCl_3$, and H_2SO_4). The lignin and cellulose concentration are calculated based only on the solid fraction remained. After pretreatment, the cellulose was liberated of almost all hemicellulose and some lignin initially present into the biomass. For the $AlCl_3$ catalyst, the higher cellulose content was attained for both temperatures (59 and 47%, respectively, after 30 min reaction time). The $FeCl_3$ poses no significant difference on recovery at both temperatures.

The results in Fig. 1 show that an increase in temperature and in the reaction time augments lignin removal. The catalyst $AlCl_3$ at 170˚C presents an increase in the removal of lignin according to the time of reaction; nevertheless, a notable difference at 180˚C is not shown. Youngran Kim et al. obtained similar results with barley for $FeCl_3$ and $AlCl_3$ catalysts at 170˚C and with a reaction time of 60 min [36].

3.2. XRD and FTIR of biomass pretreated

The XRD of biomass (nontreated and pretreated) is shown in Fig. 3. Two characteristic diffraction peaks are observed: 15.0–15.2˚ 2 θ and 22.5˚ 2 θ; characteristic

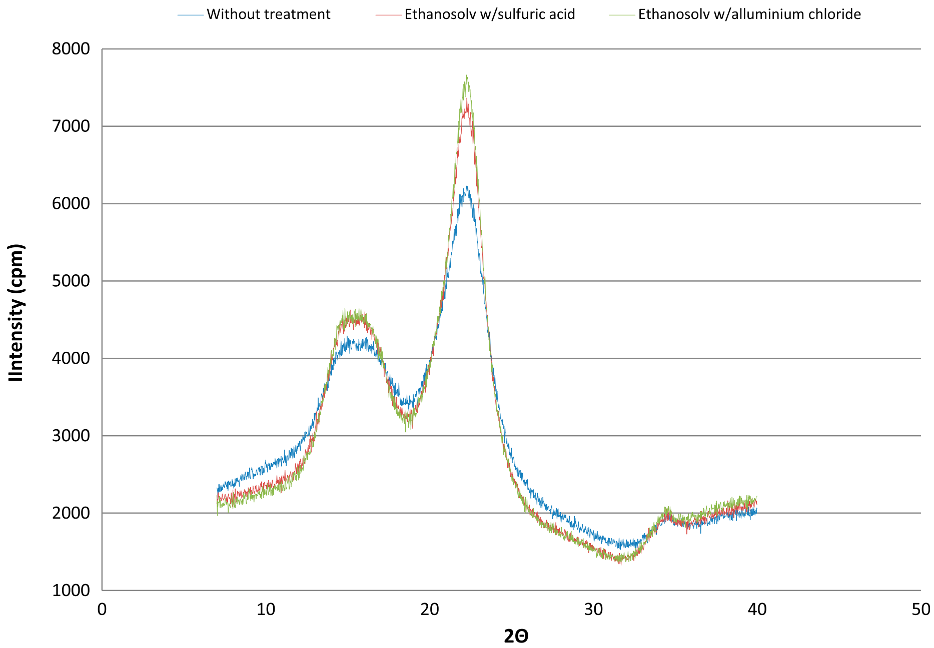

Fig. 3. XRD of sawdust and biomass pretreated by the acid and organosolv process.

to crystalline cellulose [47]. The pretreatment made did not alter the cellulose integrity and structure.

When the FTIR is analyzed (Fig. 4(a), there is an appreciable change in the carbonyl stretching region. In nontreated cellulose, there is only the 1,712 cm^{-1} band; meanwhile, for pretreated biomass, two different kinds of carbonyls are evidenced. The peak at 1,421 cm^{-1} corresponds to C–H deformation in lignin and carbohydrates. The one at 1,361 cm^{-1} is due to C–H deformation in cellulose and hemicelluloses. At 1,092 cm^{-1} the stretching of C3–OH in cellulose is observed [3,47].

3.3. Modification of cellulose

Industrially, cellulose acetate is produced mainly using the acetic acid process. The activation proceeds using in the first step acetic anhydride. The reaction is controlled by temperature and concentration of the catalyst. Sulfuric acid is added to the cellulose-acetic acid system to form cellulose-sulfate ester. The sulfuric acid and the acetic anhydride leads to acetyl-sulfuric acid, and then to cellulose sulfate ester. Finally, cellulose acetate is produced as mono, di, and tri-acetate when total acetylation occurs. Besides acetylation, degradation of the cellulose structure takes place. It is due to the interaction of the glycosidic oxygen bond of cellulose which hydrolizes in the presence of acids. During the hydrolysis, water content also affects the acetyl distribution.

The morphology of wood pulp is very complex. The pretreatment affects accessibility. The lignin and residual hemicellulose are also acetylated with an immediate effect on the properties of cellulose acetate.

Pretreated sawdust was acetylated and weight gain was attained, as it has been reported in other works [38,48]. All the weight gain during acetylation can be related to the blocked hydroxyl groups.

The acetylation performance was measured through the ester content (%ED). The ED has been determined by a complete hydrolysis of the acetylated cellulose with NaOH. Then, the excess of sodium hydroxide is back titrated with HCl. The results in our work are showed in Table 4. There were no significant differences among treatments (Tukey analysis $p < 0.05$). Tronc et al., acetylated blue agave bagasse fibers with acetic anhydride and octanoic acid and they achieved 34% ED [38]. They determined that one of the factors influencing the esterification was particle size, since esterification was also performed on the fibers. Acetylation process occurred in the entire structure, hemicellulose, cellulose, and lignin. It has been previously reported that the rate of reaction with biomass is in the following order lignin > cellulose > hemicellulose [49].

For the formation of membranes by EP, it is necessary to have acetylated cellulose, in different degrees of substitution (DS), totally dissolved. The DS is related to the acetyl content. It influences the solubility of the acetylated cellulose in different solvents. It was found

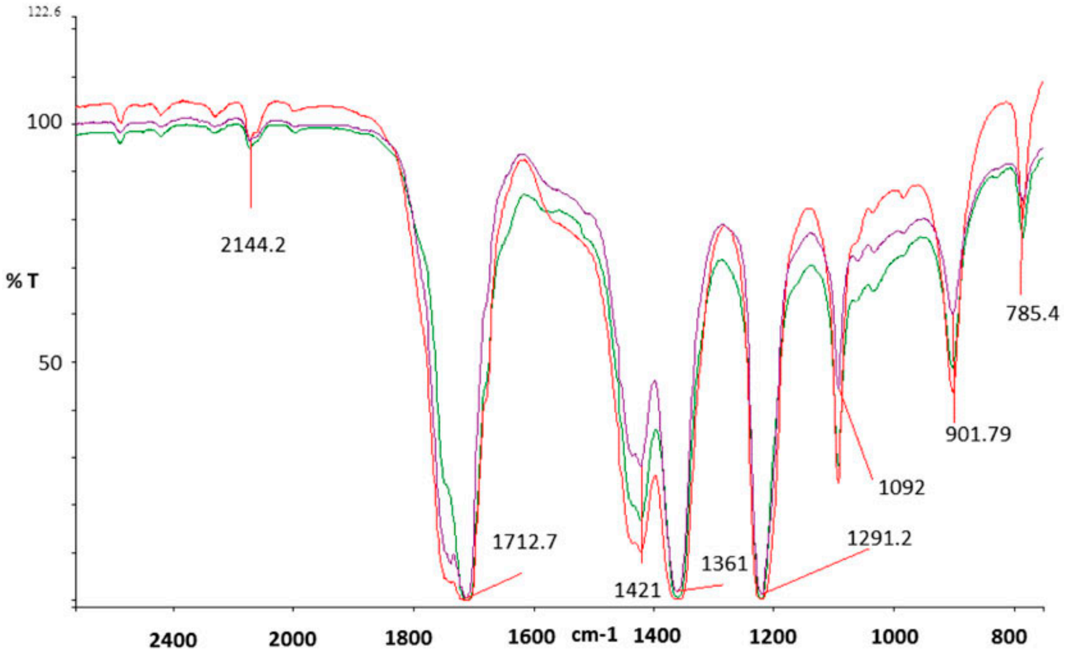

Fig. 4(a). FTIR of biomass pretreated ($AlCl_3$ purple line, H_2SO_4 red line) and untreated from *Pinus* spp. sawdust (green line).

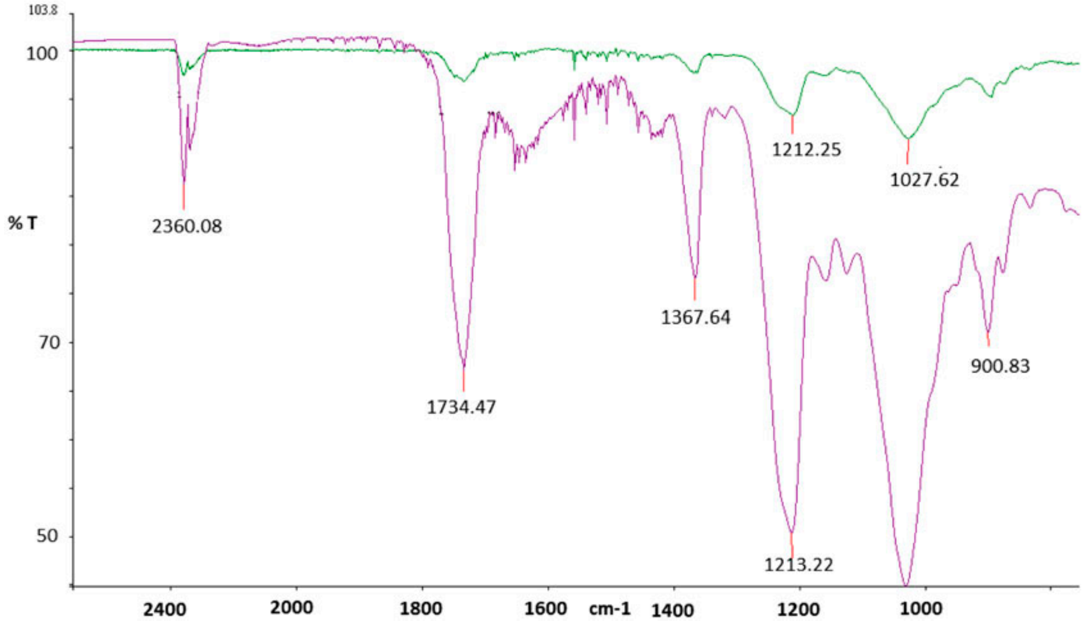

Fig. 4(b). ATR-FTIR of cellulose membranes obtained by ethanosolv (purple) and chemical pulping (green).

that cellulose acetates with high acetyl content are soluble in methylene chloride. So, we presume that mainly the highly substituted cellulose esters are forming the membrane by EP.

3.4. Membrane characteristics and operation

Several infrared spectra were acquired for all the membranes prepared. Fig. 4(b) shows two examples from sawdust pretreated by two different routes.

Table 4
Ester content in acetylated cellulose and thickness of the membrane for each condition

Pretreatment to obtain cellulose		Thickness (μm)	%ED
Pulping	120˚C	39.62 ± 1.75	27.46
Pulping and Bleaching	120˚C	25.62 ± 1.21	29.19
Ethanosolv H_2SO_4	170˚C	29.61 ± 1.1	24.42
	180˚C	34.47 ± 1.39	29.19
Ethanosolv $AlCl_3$	170˚C	32.81 ± 1.97	27.46
	180˚C	27.14 ± 1.81	25.29
Ethanosolv $FeCl_3$	170˚C	33.71 ± 1.90	26.45
	180˚C	30.14 ± 1.68	29.19

Although the spectra show different intensities in some bands, these bands correspond to the same frequency in both and were repeated in every spectra analyzed. Among the stronger bands, there is one at 1,734 cm^{-1} which corresponds to the carbonyl group (C=O) [48,49].

The band that is at 1,030 cm^{-1} belongs to the vibration of (C–O) of primary alcohols. Another band at 1,213 cm^{-1} has been reported as an extension of acetate groups (C–C=O), which characterize acetylated cellulose [4,50].

Thickness was measured by SEM and the results are presented in Table 4. Thickness was not altered by pretreatment. There is no difference among the materials prepared (Tukey analysis $p < 0.05$). Some micrographies were also obtained and no structural differences were evidenced. Only dense membranes were synthesized (Fig. 5(a) and (b)).

Table 5 shows the results of the hydrodynamic and mechanical tests done. Flux, permeability, and rejection were calculated based on the data obtained. Young moduli were obtained by Rheometry. The strain was measured as a function of stress. In the viscoelastic region, the modulus was calculated as the slope of the strain vs stress curves.

Rodrigues et al. prepared sugarcane cellulose triacetate films by casting [11]. The water vapor flux was 9.10×10^{-7} g s^{-1} cm^{-2} and this value was comparable to that of cellulose triacetates reported by Kawaguchi et al. (3.05×10^{-7} g s^{-1} cm^{-2} at 1 atm) [51]. In our work, fluxes were as high as 451.6 L h^{-1} m^{-2} bar^{-1} equivalent to 12.5×10^{-3} g s^{-1} cm^{-2} at 1 atm, and for liquid water. The same author (2007) prepared from the same raw material membranes with variable amounts of PEG [48]. They measured the water vapor flux through the membranes obtained in 18.57 Lh^{-1} m^{-2}, which varied slightly by changing the thickness of the membranes.

Other reports on the preparation of membranes from recovered cellulose are using CA from newspaper and mango seeds [12]. They acetylated the cellulose heterogeneously and the degree of substitution of CA was 2.65 ± 0.07. They used CH_2Cl_2 and water to obtain membranes by immersion precipitation. Ion diffusion was calculated in an active transport

Table 5
Flux, Young moduli (YM), and rejection of membranes obtained at different pretreatment conditions

Pulp pretreatment	Pressure, bar	Process	Flux (L h^{-1} m^{-2} bar^{-1})	Rejection Ca (%)	Rejection Na (%)	YM (Pa)
PULPING	7.6	UF	25.71	9.51	*ca* 0	297.2
PULPING/BLEACHING	9.3	UF	24.46	47.08	18.60	312.2
ET-H_2SO_4, 170˚C	5.2	MF	167.00	41.96	25.36	105.9
ET-H_2SO_4, 170˚C	9.0	MF	48.21	88.44	13.69	48.5
ET-H_2SO_4, 170˚C	9.0	UF	147.73	40.70	16.35	87.7
ET-H_2SO_4, 180˚C	4.1	MF	250.87	44.53	*ca 0*	Nd
ET-H_2SO_4, 180˚C	9.0	MF	185.39	61.81	*ca 0*	247
ET-H_2SO_4, 180˚C	9.7	MF	23.02	43.23	9.96	100.9
ET-$AlCl_{3,}$ 170˚C	4.1	MF	451.56	50.95	*ca* 0	101.1
ET-$AlCl_{3,}$ 170˚C	8.3	MF	44.21	64.98	*ca 0*	107.2
ET-$AlCl_{3,}$ 170˚C	6.2	UF	338.67	38.60	6.24	81.6
ET-$AlCl_{3,}$ 180˚C	6.9	MF	94.33	46.56	10.36	136.6
ET-$AlCl_{3,}$ 180˚C	4.1	MF	213.24	*ca* 0	76.01	112.6
ET-$AlCl_{3,}$ 180˚C	7.9	MF	215.74	69.44	26.01	162.1
ET-$FeCl_3$, 170˚C	9.1	MF	209.05	89.75	0	171
ET-$FeCl_3$, 170˚C	2.8	MF	10.45	67.63	0	275
ET-$FeCl_3$, 170˚C	7.6	MF	83.08	84.55	0	111.1
ET-$FeCl_3$, 180˚C	8.4	MF	27.13	34.73	6.92	294
ET-$FeCl_3$, 180˚C	9.0	UF	97.26	79.35	3.66	136
ET-$FeCl_3$, 180˚C	6.6	MF	120.42	78.59	19.96	112.6

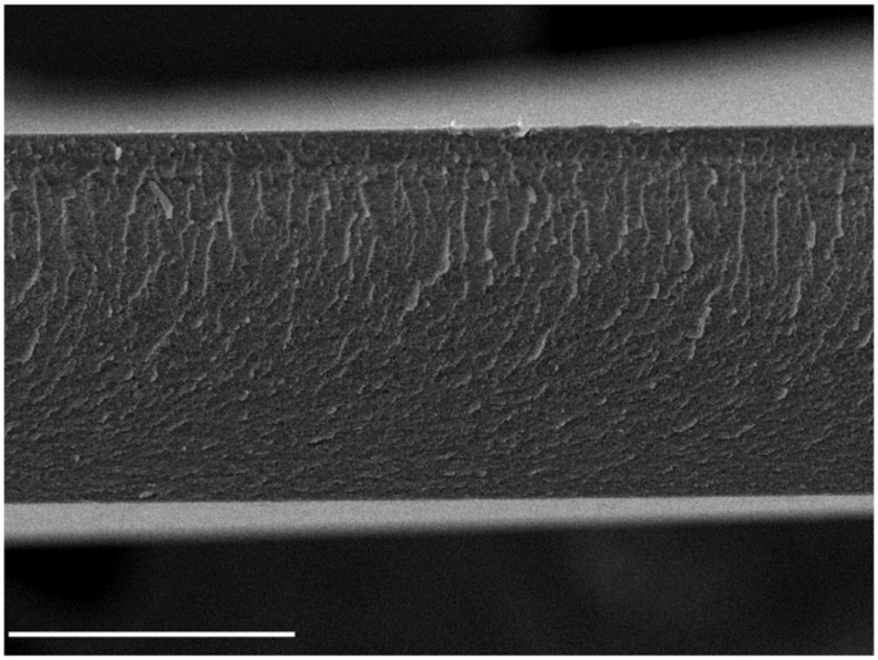

Fig. 5(a). Scanning electron microscopy (1,000×) of a selected membrane (transversal view) obtained by the organosolv treatment with $AlCl_3$ at 180°C (scale 40 μm).

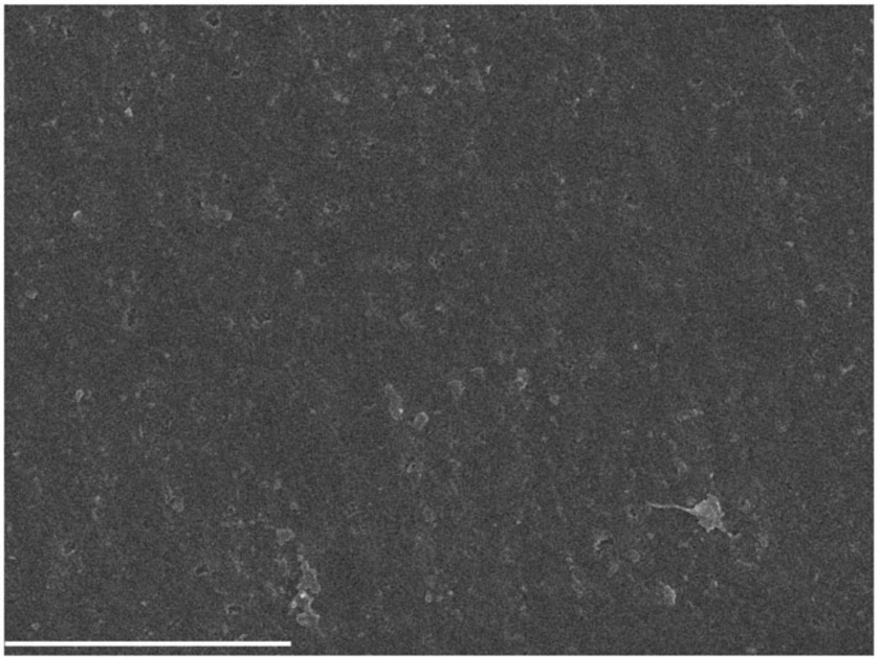

Fig. 5(b). Scanning electron microscopy (4,000×) of a selected membrane (frontal face view) obtained by the organosolv treatment with $AlCl_3$ at 180°C (scale 17 μm).

experiment, where potassium coefficient was measured as 1.82×10^{-8} cm^2 s^{-1}. No water flux was reported.

Mundim-Ribeiro et al. produced cellulose acetates with different degrees of acetylation from cellulose extracted from corn stover [52]. They obtained asymmetric membranes by immersion precipitation using a dioxane-acetone system. Their transport properties were measured using albumin in an ultrafiltration process. They presented rejection to this protein of 87.39% and 80.50% depending on the acetylation degree of their membranes.

As far as the authors know, there is no study on the use of cellulose pretreated for membrane preparation. Our results on flux determinate an ultrafiltration or microfiltration process. Rejection for $FeCl_3$-pretreated cellulose was up to 80%. This behavior only could be explained by the chemical properties of the acetylated lignocellulose, which conforms the material. Minato et al. reported that lignin elimination brings a dramatic change of the physicochemical structure of the biomass [53]. An increment in lignin reactivity and lower accessibility for holocellulose for acetylation has also been observed. Analyzing the lineal correlation among residual lignin and calcium rejection (Fig. 6) gives us confirmation on the lignin role in membrane performance. In this graph, the highest results obtained with $FeCl_3$-pretreated cellulose are not considered.

Fan et al. developed a route for the preparation of cellulose acetate membrane from ramie fiber [54]. CA was modified with polyethylene glycol and tributyl citrate. They measured the mechanical properties of their materials by dynamic mechanical analyisis. For the best membrane, they reported a 4.55% strain for a stress of 30.05 MPa. Our studies were made with the rheometer, where films were not subjected to a tensile stress but to a shear stress; thus, Young moduli (YM) refer to this kind of process. The YM is a measure of the resistance of the material to deformation. For the most resistant membrane, a strain of 17.36% was attained for a 17.8 MPa stress. Moduli range from 48.5 to 312 Pa. For instance, chemically treated cellulose generates better membranes from a mechanical point of view.

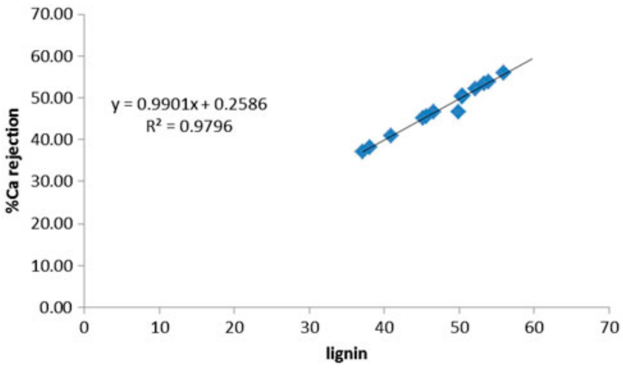

Fig. 6. Correlation between % lignin and % Ca rejection with membranes obtained by different organosolv and traditional pre-treatments.

4. Conclusions

Sawdust from *Pinus* sp. was pretreated by the ethanosolv process using three different catalysts ($AlCl_3$, $FeCl_3$, and H_2SO_4), and it was compared with traditional methods used to recover cellulose. For all of them, cellulose yield diminishes and lignin removal rises, as temperature and reaction time increase. The solid substrate with the highest concentration of cellulose was pretreated with $AlCl_3$ at 170˚C and 30 min of reaction. The removal of hemicellulose was greater than 70% for all pretreatment conditions, obtaining the best results with $AlCl_3$ at 180˚C and 30 min. On the other hand, $FeCl_3$ does not present significant differences in the content of cellulose in the substrate; however, it presents a decrease in the degree of delignification.

Chemical pulping and bleaching presented lower cellulose yields than the ethanosolv treatments. Acetylation of the biomass pretreated was evidenced by the FTIR analysis of membranes by the presence of the ester bonds at 1,734 cm^{-1} assigned to carbonyl C–O stretching of ester. ED% was almost unchanged for all the pretreatments realized, which ranged from 24.42 to 29.19%. The EP method produced symmetrical dense films. Our flux results analyzed an ultrafiltration or microfiltration process. The performance of membranes depends on the pretreatment used; where residual lignin in the acetylated material correlates with the rejection capacity for divalent ions. Rejection for $FeCl_3$ pretreated cellulose was up to 80%. This behavior only could be explained by the chemical properties of the acetylated lignocellulose which conform the material. For the most resistant membrane, a strain of 17.36% was attained for a 17.8 MPa stress. Modulii ranges from 48.5 to 312 Pa. Chemically treated cellulose generates better membranes from a mechanical point of view.

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