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Biopolymers from Waste Biomass — Extraction, Modification and Ulterior Uses

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Abstract

The residues coming from woodlands and agricultural exploitation constitute the most abundant biomass available on earth. Its importance as a source of renewable energy has grown in addition to the environmental impact. Biomass waste is a lignocellulosic feedstock which contains three main biopolymers: cellulose, hemicellulose and lignin. It could be utilized for the production of a number of value-added products due to their chemical composition, but it is necessary to efficiently recover the valuable biopolymer as intact as possible by different processing techniques. For different applications, the principal objective of pre-treatment is to keep the cellulose intact, meanwhile hemicellulose and lignin are removed. The yields of the fractions depend on the pre-treatment method, which is the most expensive step in biomass conversion. Traditionally, cellulose is obtained by kraft, sulphite and soda treatments. These methods are non-environmentally friendly and generate huge quantities of toxic wastes. Recently developed models considering the environmental laws encourage the sustainable processing of biomass into value-added products. The use of ionic liquids as new solvents for biomass waste and organosolv processes is reviewed, which are used to obtain cellulose. One of the possible applications of cellulose is membrane synthesis, which has been reported for other biomass materials, such as sugarcane bagasse, mango seed and newspaper. In this chapter, some green pre-treatment methods, different sustainable routes for cellulose modification and some of the results obtained on membrane development based on waste biomass are discussed.

Keywords: Biomass, Waste, Pre-treatment, Membranes

1. Introduction

An alarming environmental and economic situation is created by agro-industrial and forestry wastes, which are produced in large amounts annually. For example, in Mexico in 2011, sawmills produced 3.9 million m³ of wood which generated 100 tons of waste. Chihuahua has the second place in timber production with an 18.3%, in 2011 at the national level. At the state level, *Pinus* sp. (955, 654 m³ roll) and oak (51, 170 m³ roll) are widely used, of which 71.6% are used by sawmills. In 2008, there were 19, 246 m³ of waste in the genus *Quercus* (oak). Although fluctuations are reported each year and production of oak has reduced since 2007, 20–25% of the generated waste at sawmills corresponds to this genus [1]. Generally, these residues are exposed to the environment causing problems due to the suspension of particles of sawdust in the air. These residues are used for the production of pellets; however, the amount of bioaccumulation is very large and hence this technique cannot be applied. Generally, sub-products are used directly as a fuel or to manufacture agglomerated materials, but this usage is not enough to overcome the problems of its disposition.

Another interesting subproduct is the agave bagasse. The raw material to produce tequila with 'Denominación de Origen' (denomination of origin) is agave tequilana. Bagasse is the final waste produced after the head of the plant is cooked and pressed to extract the sugar liquor which will produce tequila by fermentation of *Saccharomyces cerevisiae*. According to the National Consortium of Tequila, 350, 000 tons of bagasse waste on a dry basis is produced annually compared with 14.1 million litres of tequila produced in 2012. The use of agave bagasse as a resource helps to reduce environmental degradation that is caused by the accumulation of the tequila waste. These compounds are accumulated and disposed in large volumes and are resistant to degradation, and they are stored for 6–8 years [2]. For instance, using the bagasse from agave tequilana is very helpful, from an economic and environmental point of view.

Biomass waste, as a lignocellulosic feedstock, contains three main biopolymers: cellulose, hemicellulose and lignin. Due to their chemical composition based on carbohydrates, they are used for the production of a number of value-added compounds. Many processing alternatives are being studied to efficiently recover biomass polymers. The main purpose of pre-treatment is to remove as much hemicellulose and lignin as possible, while simultaneously keeping enough cellulose undamaged [3]. Fractions with a high yield of cellulose depend on the pre-treatment method, which 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. Cellulose is currently separated from lignocellulosic materials using non-environmentally friendly processes, such as kraft, sulphite and soda treatments, with the consequent generation of toxic wastes. In the last few years, new rules have been framed due to the growing restrictions in the environment, based on the sustainable processing of biomass into value-added products [4]. In this chapter, traditional and environmentally friendly methods for biomass pre-treatment are reviewed, with special emphasis on the use of green technologies [5, 6]. A brief description about nanostructured composites used as membrane materials is provided. Some results obtained using agave bagasse and sawdust are also highlighted.

2. Materials of cellulosic origin: pre-treatment and new treatments of biomass for obtaining cellulose

Residues from biomass consist of three macromolecular components: cellulose, lignin and polyoses as well as small quantities of extractives and mineral salts, having a lamellar structure in which the components are distributed.

The cellulose and hemicellulose are predominant in the region of the cell wall, and lignin is distributed throughout the structure, presenting a maximum concentration at the middle lamella. The transformation processes of lignocellulosic fractions are limited by the structure of the biomass.

Generally, the breakdown of the complex cellulose–hemicellulose–lignin or its fractionation by pre-treatment techniques and delignification are required [7]. Cellulose (Figure 1) is a polymer formed by long linear chains of glucose residues linked by beta-D-glucose bonds, where the glucose molecules are linked through carbons 1 and 4 to form cellobiose; 1–4 hydroxide link occurs at the β -position (equatorial), resulting in the formation of a linear polymer. Hemicellulose is approximately 25% of the biomass, and it is a linear polysaccharide polymer similar to cellulose, except that it is primarily composed of xylans, glucomannans and arabinose. Another difference is that the resistance is lower due to its degree of polymerization (70–200 units). Like cellulose, it is a polar molecule and therefore contributes to the polarity of the wood. Hemicelluloses contain various residues of sugars, generally from two to four or up to six.

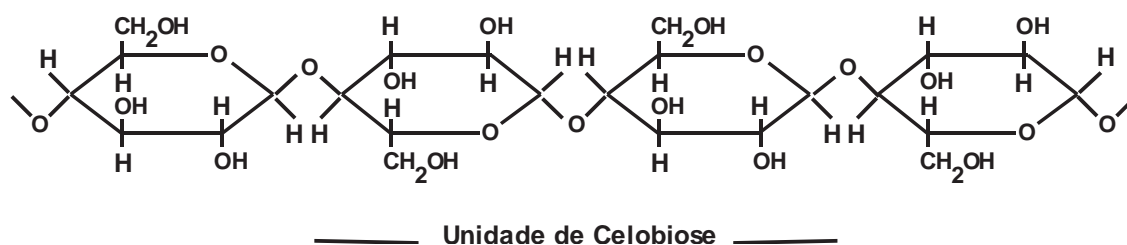


Figure 1. Structure of cellulose; central part of the molecular chain [8].

Lignin is a highly stable macromolecule, being the second most abundant biopolymer, after cellulose. Lignin is primarily composed of α -phenyl propane units forming an amorphous tridimensional macromolecule, representing 20–30% of the total mass of the lignocellulosic material. The structure of lignin is attributed to its biosynthetic mechanism, which is processed via radicals from precursors such as sinapylic, coniferyl and p -coumarylic alcohols. The following are the most abundant types of bonds formed between the phenylpropane units: β -O-4 e α -O-4 (50–65%), β -5 (6–15 %), β -1 (9–15%), 5 (5–9 %) y β - β (2–5%).

Cellulose is one of the most common biopolymers representing about 1.5×10^{12} tons of total annual production of biomass. It is regarded as an inexhaustible raw material for the production of eco-friendly and biocompatible products. The wood pulp is the most important for processing cellulose, which is aimed at the production of paper and paperboard source.

Approximately 2% was used for the production of regenerated cellulose fibres, films and for synthesizing many cellulose esters and ethers [9]. These derivatives, produced on an industrial scale, are used in optical films, portion means, additives, pharmaceuticals, cosmetics and coating, among others [7]. In its polymeric form, it can be used for papermaking or converted into derivatives such as acetyl cellulose, nitrocellulose, ethanol, artificial fibres, colloids with medicinal uses, celluloid, various plastic materials and also in obtaining esters and cellulose ethers.

Several studies have shown that it is possible to obtain cellulose from agro-industrial waste, such as waste from fibre, bagasse and wood [10, 11]. However, the cellulose obtained from this resource has viscosity values unsuitable for papermaking. One option for using it is to chemically derive it for compounds that can be commercially exploited. To obtain cellulose from agro-industrial waste, the separation of macromolecular components should be carried out by chemical, physical or enzymatic processes.

The modification of cellulose has been widely studied due to the possibility of obtaining compounds with a wide industrial application. These modifications include the production of cellulose esters, with applications ranging from auxiliaries in large-scale polymerization, the viscosity thickeners in cosmetics, foods, drugs and membranes. Also, the study of the use of lignin has both economic and environmental importance due to the wide availability of the same from agro-industrial wastes.

There are several processes of delignification in the treatment of biomass. Most of them are based on the previously optimized methods for the delignification of wood. The main industrial processes of chemical delignification of lignocellulosic materials are the kraft, soda and sulphite processes, which release large amounts of toxic chemicals to the environment [12]. The complex cellulose–hemicellulose–lignin must be fractionated by pre-treatment to remove maximum lignin, by not weakening too much the cellulose fibres.

The kraft method stands out among all other chemical pulping processes due to its high efficiency in lignin removal, without damaging much of the cellulose fibres. Of all the methods, this method is used in 60% worldwide [8]. The kraft process uses sodium hydroxide and sodium sulphate in large digesters to which splintered wood is introduced ; this process removes maximum lignin leaving a brown paste; however, it produces toxic emissions such as sulphur dioxide (primary contributor to acid rain). A black liquor is obtained that burns modern plants, generating vapours that can be used for generating electric energy. Waste water is also treated, purified and recycled to regenerate sodium sulphide and caustic soda.

Another method used is the 'sulphite', where a clearer, weak and soft paste is produced. Similar to the kraft method, the chemicals used can be recycled, but the recovery efficiency of sulphuric acid is lower, and also a higher amount of sulphur dioxide is released per ton of the pulp produced.

Unlike traditional industrial pulping methods, processes using techniques of steam explosion and organic/water solvent mixtures (organosolv) or their combination allow the use of not only the cellulose but also the lignin and polyoses for the production of various chemical inputs, also being environmentally friendly routes [7].

Organosolv process has been investigated to extract lignin from pulp for paper production. In this process, an organic or aqueous organic solvent is mixed with a catalyst (usually an inorganic acid such as HCl or H₂SO₄) to break the bonds of the lignin and hemicellulose [13]. Organic acids as catalysts can also be used, such as oxalic, salicylic and acetylsalicylic acids. Table 1 shows some of the pre-treatment processes, their advantages and limitations.

Pretreatment	Advantage	Limitations
Steam explosion	Causes degradation of hemicellulose and lignin transformation; effective cost.	Incomplete disruption of lignin-carbohydrate matrix.
Fibre explosion with aqueous ammonia	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	Increases the accessibility area, does not produce inhibitors for subsequent processes.	Unchanged lignin or hemicellulose
Ozonólisis	Reduces the lignin content; don't produce toxic waste.	Large amounts of ozone are required, it is an expensive process
Biological	Degrades lignin and hemicellulose; low energy requirement	The hydrolysis speed is very low
Organosolv	Hydrolyzed lignin and hemicelluloses.	Solvents need to be drained from the reactor, evaporated, condensed, and recycled: high cost.

Table 1. Pre-treatment processes. Advantages and limitations.

The objective of pre-treatment is to remove the maximum amount of lignin and hemicellulose as possible, while maintaining the cellulose intact. Typically used solvents are methanol, ethanol, acetone, ethylene glycol, triethylene glycol and phenol. The name ethanosolv refers to an organosolv process with ethanol. The ethanosolv method is more convenient than other pre-treatments because it is safer, since ethanol is less toxic than other solvents [13].

In addition to the advantages presented in Table 1, organosolv pre-treatment has the following benefits: 1) organic solvents are easily recovered by distillation and can be recycled back to the pre-treatment process; 2) after pre-treatment, the recovered lignin can be used for various co-products (vanillic acid, vanillin and p-coumaryl); and 3) pre-treatment contemplates the use of all components of the biomass, making it viable for biorefinery of lignocellulosic biomass. The ethanosolv process is currently one of the best pre-treatments of biomass residues from an environmental perspective [14–21].

At the top of the development of innovative methods for pulping, it was found that the ionic liquids (ILs) were the most studied solvent in the last decade [7, 12, 22–26].

The first report of ionic liquids as non-derivatizing solvents of cellulose was published in 1934 by Charles Graenacher. He applied the N-alkylpyridinium salts for dissolving cellulose and a homogeneous reaction medium [24]. However, it was in 2002 when Swatloski reported the use of comparable salts with boiling points below 100 °C, currently known as ionic liquids, provoking a new start in the research of cellulose. It has been observed that the most promising ILs for the modification of cellulose are salts of 1-alkyl-3-methylimidazolium [27–29].

To date, much is known about ILs: organic salts with low melting point, of which those containing ammonium, pyridinium and imidazolium are the most suitable for dissolving cellulose, in other words, those organic salts with asymmetric cations to interact appropriately with the skeleton of cellulose.

A generally accepted theory to explain the interaction between the ionic liquid and polymers has not been proposed. Such solvents are considered non-derivatizing solvents, i.e. with non-covalent bonds, as shown in studies of ^{13}C nuclear magnetic resonance (NMR). These studies indicate that the chloride interaction is higher for the breaking the hydrogen bond, than in the cation, as in the DMAc/LiCl systems.

The most widely used ionic liquids, with melting temperatures below 55°C, and extremely low viscosities, include the AmimCl (1-allyl-3-methylimidazolium chloride) and EMIMAc (ethyl 1-ethyl-3-methylimidazolium acetate). These are considered as non-toxic, non-corrosive and biodegradable. Therefore, the use of ILs for extracting cellulose from waste is of particular interest for the development of green methods for obtaining this vegetal biopolymer.

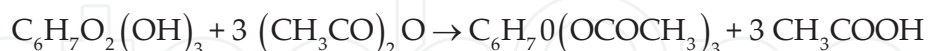
Another method for biomass waste treatment processes is solid-state fermentation, in which lignolytic fungi and/or the enzymes that they produce are used [14, 30–33]. These are better known as techniques of biopulping or biobleaching, if xylanases or laccases are used. A fermentation process in solid phase is defined as the one occurring in the absence or almost nule presence of water, using natural and inert substrates as solid supports. The substrate supplies nutrients to microbial growth, and it serves as a means of attachment of cells. Among the most important factors for the growth of microorganisms are the particle size, the level of water and humidity. White rot fungi, such as *Phanerochaete chrysosporium* and *Ceriporiopsis subvermispora*, are the most important [14, 30–33]. However, the main limitations are the long incubation times thereof, two to four weeks, and the yield loss, because the fungus attacks the polysaccharides simultaneously.

Therefore, there is a current area of research on the biotechnological processes using enzymes instead of fungus [34]. The enzymes added directly, such as the lignin peroxidase complex, into the biomass showed better pulping yields.

3. Chemical modification of cellulose

By the chemical treatment of cellulose, different compounds can be obtained with new and particular features, including hydrophobic compounds, water-soluble products, thickeners, ion-exchange materials resistant to the action of microorganisms, etc. In these chemical

modifications, cellulose ethers, such as methylcellulose (MC), hydroxyl propyl methyl cellulose (HPMC) and cellulose acetate, are mainly included. The esterification of the cellulose in acetic acid is not possible and therefore cannot be used as an esterifying agent. Typically, acetic anhydride is used as an acetylating agent. This acetylation reaction of cellulose with acetic anhydride can be represented by the following equation:



If the reaction is only performed with acetic anhydride, esterification is very slow; therefore a catalyst is needed. The most commonly used are sulphuric or perchloric acid. Acid-catalyzed treatments have many limitations. First, the acid itself is not environmentally friendly reactive, and its discharge can cause environmental pollution. Second, its corrosivity requires expensive construction materials, which increase the cost of the process [35].

The esterification of cellulose using ionic liquids is an area of current development [10, 36, 37].

The main advantage of the process is that a regioselective esterification can be obtained. The direct esterification with highly sterically demanding acylating reagents has been studied with substances such as pivaloyl chloride and adamantyl and 2,4,6-trimethylbenzoyl of cellulose in solvents such as DMAc/LiCl, DMSO/TBAF and AmimCl [27].

In 2011, Wang reported the direct extraction of cellulose with AmimCl, with an 85% yield of cellulose initially contained in the fibre, using the DMSO/water system as the precipitant [36]. Esterification in this medium can be performed in one step from the cellulose fibre, obtaining cellulose acetates with 2.16–2.63 degrees of substitution (DS) of. The major advantage of the process is that it involves a one-step preparation. In a homogeneous medium, the DS can be easily controlled by adjusting the time of acetylation, as acetylated products may be obtained according to the needs of synthesis.

4. Preparation and characterization of membranes

The membranes have overcome many shortcomings of conventional separation methods because of features such as ease of operation, energy advantages, selectivity and low operating costs. Through selective complexation reactions (reactive membranes) and processes of ultra-, micro- and nanofiltration (inert membranes), we have been able to make highly specific separations [38]. Currently, they are the basic materials that stimulate scientific research and technological development.

The membrane is clearly the most important part of the separation system. A membrane is a permeable or semi-permeable phase, which divides two fluid phases: feeding (F) and recovery (S). It is essentially a barrier that allows the selective passage of the chemical species, controlling the relative speeds of transport, which ideally produces a phase (F) without the transported components and a phase (S) enriched with them. The operation of a membrane, therefore, will

depend on its structure, largely determining the separation mechanism and its application. For this reason, the science of membranes has clearly focused on the development of materials with different properties such as synthetic polymers, modified natural products, inorganic membranes, ceramic, metal and liquids [39–41].

The flow across the membranes is possible when a directive force is applied, as concentration gradients, temperature, and pressure or electrical potential.

This parameter is used as a criterion for the classification of membrane processes that exist; for example, ultra-, micro- and nanofiltrations are carried out thanks to a hydrostatic pressure gradient, distillation by membrane is due to a temperature gradient, and due to concentration gradients processes of pervaporation, dialysis and reactive liquid membranes transportation are achieved.

In general, the membranes are classified into three: inert, reactive and composite. An inert membrane is one in which any chemical transformation is not seen involved in the membrane during separation, whereas in a reactive membrane, the chemical interaction between the chemical of interest and the reactive component of the membrane determines the process transport. In a composite membrane at least two types of materials are identified; one of them can be reactive and the other inert, that is the reason why a 'hybrid' transport occurs in the system.

In the processes of ultra-, micro- and nanofiltration, inert membranes of certain physicochemical properties are generally used. Depending on the application, it is necessary to control the distribution and pore size, because the transport process is related to a molecular sieving.

The filtration membranes can be easily obtained by phase inversion method. This is a process by which a polymer is transformed in a controlled way (at fixed conditions of temperature, humidity and pressure) from a liquid to a solid state. The transition to solid can be adjusted so that the morphology of the membrane can be determined. A widely used method for the synthesis of membranes is precipitation by controlled solvent evaporation [42, 43].

Generally, the cost of operating a membrane process depends on the material that the membrane contains. For this reason, it is extremely important to find new synthesis routes that are economically feasible and environmentally friendly, to obtain membranes. This study is intended to produce composite membranes from various lignocellulosic materials, in a novel way, particularly from agro-industrial wastes.

Acetylated cellulose can be regenerated by ILs solutions by precipitation in a wide variety of non-solvents, including water, alcohols and acetone. If the membrane casting is made simultaneously, an adjustment of the topographical and morphological characteristics can be attained. A large amount of work has been reported using ILs as an alternative to the traditional methods of obtaining membranes [10, 11, 37, 44–48].

The formation of cellulose acetate membranes via phase inversion using ionic liquids such as (thiocyanate 1-butyl-3-methylimidazolium) and solvents such as [BMIM] SCN, 1-n-butyl-3-methylimidazolium thiocyanate [49] has been studied. The process is compared to phase inversion in water using N-methyl-2-pyrrolidone as a solvent and acetone. It is found that the

ionic liquid has distinct effects on the process of phase inversion and in the morphology of the membranes obtained by comparing the process with NMP, N-Methyl-2-pyrrolidone and acetone due to its viscous nature.

5. Recent advances in membrane synthesis using biomass waste

As mentioned above, agave bagasse and sawdust are biomass wastes which can be revalorized by obtaining new membrane materials. Results on the organosolv treatment of *Pinus* sp. sawdust have been recently reported [42]. The following graph relates the rheological behaviour of the membranes obtained using the acetylated cellulose by the organosolv pre-treatment of sawdust.

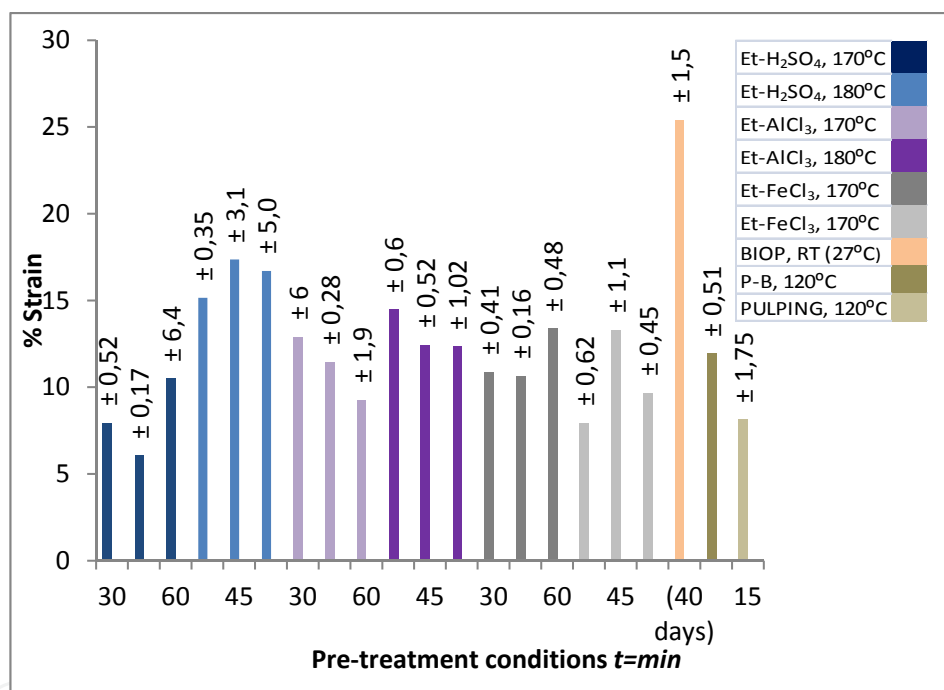


Figure 2. Percentage strain of membranes of acetylated cellulose. Cellulose was recovered by organosolv pre-treatments stated in the figure, such as ethanosolv-H₂SO₄, i.e. using sulphuric acid as catalyst and so on; BIOP refers to biopulping using *Phanerochaete chrysosporium*, P-B refers to pulping and bleaching and pulping to the traditional method using 10% sulphuric acid at 120°C.

Strain was recorded at an angular velocity of 6,286 rad/s. Strain was modified by the cellulose recovery profile. Biopulping, the longest pre-treatment performed, gave the best cellulose for membrane resistance. Materials obtained were mainly dense (Figure 3). These can resist up to 9.1 bar, addressing a micro- and ultra-filtration with the rejection of calcium in the range of 9.51–89.75%.

Similar pre-treatments were applied for agave bagasse. Membranes were obtained as shown in Figure 4. Cellulose was obtained by a traditional method using 10% sulphuric acid at 120°C

as mentioned elsewhere [48]. Acetylation was also performed using the Fischer method, and acetylated cellulignin was recovered with dichloromethane. This solution was the medium for casting at different evaporation temperatures and humidity. These materials attain nanofiltration pressure and flow conditions.

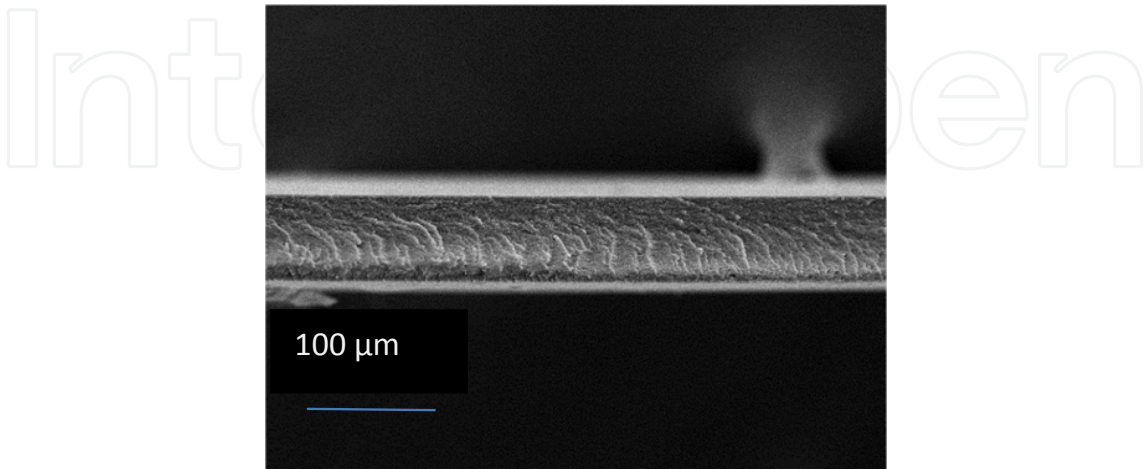


Figure 3. Scanning electron micrograph of membranes manufactured by acetylated cellulose of *Pinus* spp. saw dust.

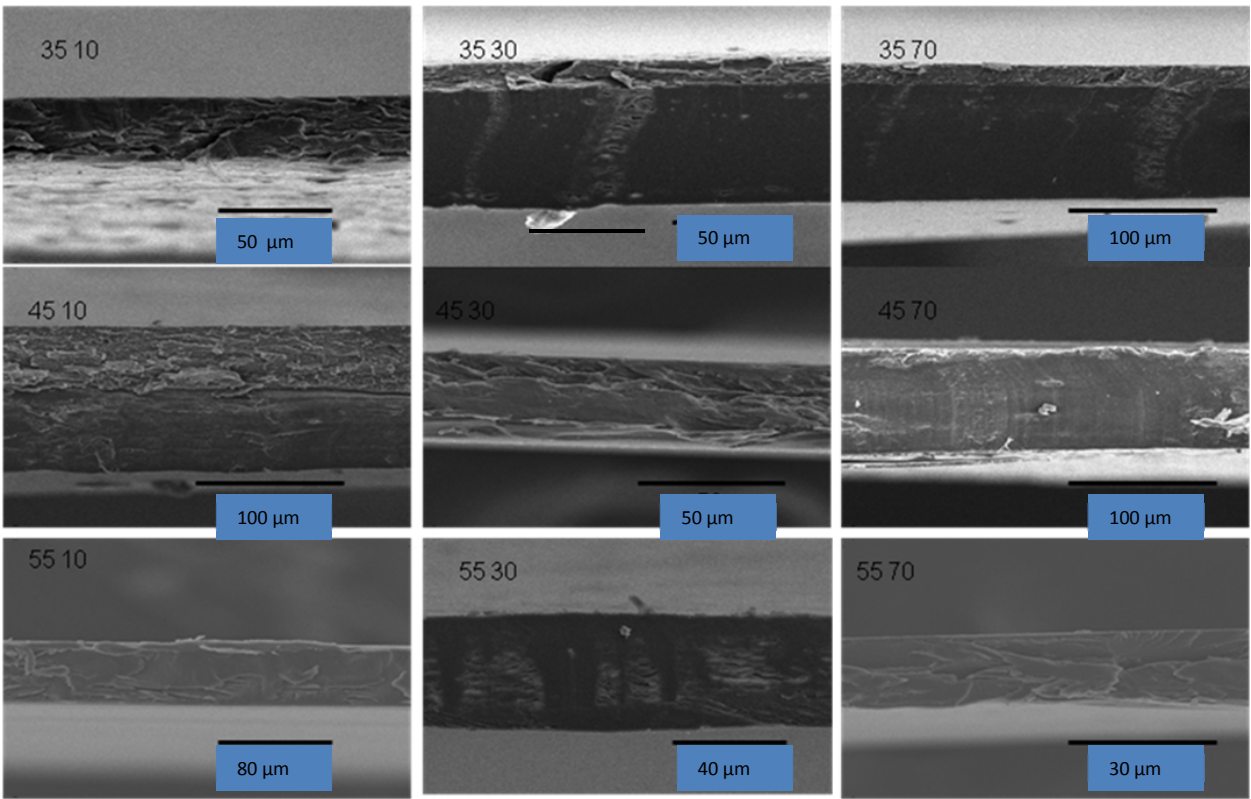


Figure 4. Acetylated cellulignin membranes from agave bagasse. Numbers on the left corners represent the following: The first two correspond to temperature (°C), i.e. 34, 45, 55; the second two correspond to humidity (%), i.e. 10, 30, 70.

6. Conclusion

Biomass waste provides an extraordinary source of biopolymers susceptible to transformation and revalorization, such as cellulose acetates, which can be further used as raw materials for membrane production. With the application of new environmental regulation for green technologies, these can even be obtained by the use of ionic liquids.

Biomass pre-treatment is a fundamental step for biomass utilization. Organosolv processes release good-quality cellulose, which can be further functionalized for other applications such as the generation of acetylated cellulignin. It could also be a good alternative to implement ILs or biological routes for cellulose recovery.

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