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Chapter

Alternatives for the Management of Industrial Forest Waste: Energy, Bioethanol, and Cellulose Pulp

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Abstract

Modern kraft pulp mills generate solid waste of 1–2% of incoming debarked wood. Given the size of these plants, with an annual production capacity of at least 1000,000 tons, each plant generates 20,000–30,000 dry tons of waste per year. The largest current use of these residues is for combustion in biomass boilers for steam and power generation. However, the conversion of biomass into biofuels and chemicals is gaining interest due to increasing demands for energy, limited sources of fossil fuels, and growing concerns about the environmental impact of greenhouse gas emissions. This chapter shows the laboratory-scale results of the use of eucalyptus wood wastes to obtain cellulose pulp by alkali pulping reinforced with hydrogen peroxide to obtain alkaline peroxide mechanical pulp or cellulosic bioethanol. Based on the results, an industrial-scale techno-economic analysis of the processes is presented and compared with current alternatives for energy generation.

Keywords: eucalyptus residues, APMP, bioethanol, valorization, industrial forest waste

1. Introduction

Although waste prevention is normally the first option to avoid later problems in waste management, forest industrialization generates a large amount of wood residue. In the mechanical transformation of wood (e.g., sawn wood, plywood), 30–50% of the logs are not part of the final product (e.g., bark, sawdust, under-sized logs, knots, chips, etc.). Depending on the size and characteristics of this waste and the integration of the wood industrial sector, it will normally be used to produce pulp, boards, or other value-added products, and it can be used as raw material for steam and power generation [1–4].

In modern pulp mills that apply the best available technologies, 1–2% of the input wood is discarded as pin chips and fines, which are formed during the chipping process and cannot be used to produce commercial cellulose pulp due to their small

size [5]. For older mills, the discarded fraction could reach 5–10% [6]. These residues, as well as waste from mechanical transformation industries, are normally burned for steam and power generation.

Direct combustion of biomass in steam boilers is a mature, proven technology for converting biomass to energy. The technology choice largely depends on the specific size of the boiler. Newer solid-fuel-fired boilers with a capacity over 15 MW are fluidized bed boilers, moving grate boilers, or pulverized fired boilers [7, 8]. Small-scale cogeneration plants (with a capacity lower than 15–20 MW) are globally widespread, and their size is normally determined by the local availability of biomass. However, the high capital cost of electricity generation and the small price gap between biomass logistics costs and electricity prices often make them less competitive [7, 9].

The main objective of this chapter is to analyze an alternative to industrial forest residues, in the understanding that their disposal through the generation of electrical energy is a process that will no longer be profitable in the future since it has higher costs than electricity production from solar or wind energy.

Alternatively, lignocellulosic biomass constitutes a material with many possibilities for the development of bioproducts and/or biofuels. It mainly comprises cellulose, hemicelluloses, lignin, and a minor fraction of extractives and inorganic compounds. Pretreatments are required to separate components to use lignocellulosic materials. Within the different chemical pretreatments, alkali is used because it has several desirable characteristics. Alkaline methods mainly use noncorrosive chemical products, and in many cases, reagent recovery is feasible due to the consequent economic and environmental advantages.

One strategy for sustainable development is to establish an economy based on the use of biomass (a “bioeconomy”)—a renewable resource that should be obtained through a production system that preserves the environment. This requires an increase in products’ availability and their corresponding production technologies to simultaneously substitute fuels and materials derived from fossil sources (“economy decarbonization”). This concept can be developed through a biorefinery approach that comprises sustainable biomass processing into a portfolio of marketable products through the combination and integration of different processes. A biorefinery using lignocellulosic materials of forest origin to obtain biofuels and other products contributes to better meeting sustainable development goals related to energy, industry, innovation, infrastructure, and climate. Bioethanol production from lignocellulosic materials as a substitute for gasoline allows the increased incorporation of renewable energy in transport without too many changes in the current infrastructure and engines, facilitating the transition toward decarbonization of this sector.

Obtaining ethanol requires a biomass pretreatment that improves the accessibility and susceptibility of cellulose for enzymatic hydrolysis (cellulases) to glucose, preventing degradation of carbohydrates and the formation of byproducts’ inhibitors of hydrolysis and fermentation processes. This allows for both the fractionation of hemicellulose components and the recovery of lignin. Alkaline pretreatment uses sodium, potassium, calcium, or ammonium hydroxides as reagents and is typically performed at lower temperatures than acid or hydrothermal pretreatment. Sodium and calcium hydroxide (lime) are the most common reactants (conc. 0.05–0.15 g_{hidroxi}/g_{biomass}), although recirculating ammonia percolation or fiber explosion/expansion treatments by ammonium are also common. Pretreatment with sodium or calcium hydroxide is normally carried out at temperatures between 20 and 130°C, with reaction times ranging from minutes to hours or days, depending on the working

temperature [10–12]. In materials with a high lignin content, such as wood, this pretreatment is less efficient, so its use is more common in agricultural and agro-industrial waste [12].

In alkaline hydrolysis, fiber solvation occurs, producing swelling. The intermolecular ester bonds that cause the cross-linking of the chains are saponified, opening the structure of the hemicelluloses and lignin, and splitting the glycosidic bonds of the hemicellulose chain. Acetyl and uronic groups also react with alkali, separating them from the fiber. Depending on the applied conditions, the depolymerization of lignin molecules can occur by cleavage of the internal molecular bonds of the α and β -aryl ether type, which contributes to the degradation of lignin. All of these changes improve access to the cellulose chains, which become less crystalline with the treatment by reacting to the hydrogen bonds that link them. Under conditions of greater intensity, “peeling” reactions of the hemicellulose and cellulose chains may occur, causing a decrease in the degree of polymerization [10, 13, 14].

Among alkaline pretreatments, an alternative is the addition of an oxidizing agent (oxygen or hydrogen peroxide [H_2O_2]) to the alkali. The reaction mechanism is similar to alkaline hydrolysis, but it is aided by an oxidative effect on lignin, increasing its splitting from the lignocellulosic biomass. Alkaline peroxide treatments have faster kinetics at low temperatures, thus presenting technological and economic advantages over conventional alkaline treatments [10, 12].

Alkaline peroxide mechanical pulp (APMP) production is a particular case within alkaline treatments at low temperatures. It consists of treating wood with sodium hydroxide (NaOH), H_2O_2 , and stabilizers at temperatures below $100^\circ C$, during which simultaneous pulping and bleaching occur. The pretreated material then goes through the mechanical defibration and refining stages [15, 16]. This type of pulping is widely used in China as a process for obtaining semi-chemical pulps from wood and nonwood materials [17].

In this work, the main destination of pulp is as a filler in the production of paper, particularly tissue. There is evidence that the substitution of kraft pulp for high-yield pulps of up to 30% improves the final product's properties, providing increases in bulk, tensile strength, bending stiffness, internal bond strength, and elasticity modulus [18].

Likewise, several reports have applied alkaline pretreatment to various types of biomasses [19, 20] to improve subsequent enzymatic hydrolysis for the production of bioethanol [21, 22] or to extract hemicelluloses prior to kraft pulping [23, 24]. More recently, the use of alkaline treatment for the extraction of hemicelluloses to prepare xylan films and the extraction of hemicelluloses from commercial pulps to produce nanocellulose have been reported [25, 26].

Once the lignocellulosic matrix is broken, it is necessary to hydrolyze the cellulose to glucose, which is fermented to produce bioethanol. Cellulose hydrolysis is preferably carried out enzymatically to minimize further inhibitions caused by the coproducts of chemical hydrolysis. The hydrolysis of cellulose into glucose through an enzymatic process involves several cellulases that act synergistically: 2 exo- β -glucanases or cellobiohydrolases (CBH: CBH I and CBH II), endo- β -glucanases (EG: EG I, EG II, EG III, and EG V) and a β -glucosidase (βG) [27]. EG and CBH break down cellulose into smaller polysaccharides. EG first randomly breaks internal glycosidic bonds, then CBH I cleaves sugars from reducing ends, while CBH II cleaves cellulose toward nonreducing ends. This second stage occurs in the liquid phase and is mainly due to the hydrolysis of cellobiose to glucose by β -glucosidase [24]. The enzyme dose needed to reach an acceptable percentage of glucose and ethanol yields strongly depends on the

raw material and pretreatment used [11]. The kinetic effects on the enzymatic saccharification of lignocellulosic are largely related to the presence of polymers and nonionic surfactants, which are partially associated with the removal of lignin and cellulase stability and activation [28].

The microorganism used in fermentation must have certain conditions: high ethanol yield, high productivity, and tolerance to high concentrations of ethanol and sugars. It is also desirable for them to work in the presence of sugar degradation compounds, which are commonly fermentation inhibitors. Furthermore, it is expected that these microorganisms will have resistance to high temperatures and fermentable sugar. The most used microorganism for bioethanol production on an industrial scale is the yeast *Saccharomyces cerevisiae*, which efficiently ferments hexoses and disaccharides, such as sucrose and maltose. However, it cannot metabolize pentoses, such as xylose and arabinose, which are components of hemicelluloses [11].

The aim of this work was to compare three alternative uses for small-sized industrial forest residues. Therefore, an alkaline pretreatment reinforced with H₂O₂ was used for the subsequent production of bioethanol or bleached semichemical APMP. Based on the laboratory-scale results, an industrial-scale techno-economic analysis of the processes is presented (based on a plant located in Uruguay) and compared with current power generation alternatives.

2. Materials and methods

2.1 Raw materials

Pin chips from a local Eucalyptus pulp mill were received, dried and stored in airtight plastic boxes. The particle size distribution and chemical composition are presented in **Table 1**. Material below 0.50 mm was discarded.

2.2 Alkaline pretreatment

The process began with the mechanical impregnation of the pin chips with the pretreatment reagents in a device specially designed for this purpose. They were then transferred to a reactor where pretreatment occurred. The treated pin chips were

Component	Amount (%)	Method	Particle size distribution	
Glucan	42.0 ± 1.8	NREL\TP-510-42,618	Above 3.36 mm	7.6%
Xylan	14.1 ± 0.2		3.36–1.40 mm	43.7%
Acid insoluble lignin	20.1 ± 1.2		1.40–1.19 mm	38.0%
Acid soluble lignin	3.2 ± 0.1		1.19–0.50 mm	10.7%
Acetyl groups	2.9 ± 0.2		Below 0.50 mm	4.1%
Arabinan	1.0 ± 0.1			
Ash	0.7 ± 0.1	NREL\TP-510-42,622		
Extractives in ethanol and water	4.3 ± 0.1	TAPPI T 204 cm-97		

Table 1.
Raw material composition and particle size distribution.

refined in a disk refiner, and the resulting pulp was divided into two groups. One part was used to produce the APMP. For this, a two-stage bleaching sequence was carried out using (1) ethylenediaminetetraacetic acid (EDTA) and (2) H_2O_2 . Then, the papermaking properties of the obtained pulp were determined. The pulp obtained from refining was subjected to an enzymatic hydrolysis process, and the liquid obtained was fermented to produce bioethanol. This process is outlined in **Figure 1**.

According to Kruzolek [16], pressure is essential to achieving proper impregnation. For this, a device was designed and built to allow the pin chips to be immersed in water and reagents. By applying pressure, the occluded air in the pores was eliminated. The device was then returned to atmospheric pressure, achieving a “sponge effect” by expanding the compressed material and simultaneously absorbing the impregnated liquor. The apparatus is shown in **Figure 2**. The reagents ($NaOH$ and H_2O_2) and water were externally heated to $80^\circ C$ in a container. The amount of water was calculated to achieve a liquid-to-dry solid ratio of 7. The device, with the pin chips inside, was placed in a container within the press. Pressure was applied until it reached 0.5 MPa, held for 10 minutes, and then released.

Once the impregnation process was complete, solids and liquids were transferred to a 3 L Parr reactor (model 4522 M) and instrumented with temperature control and agitation, where the process temperature was reached using a defined heating ramp. The pressure in the reactor was maintained at 0.8 MPa using nitrogen gas.

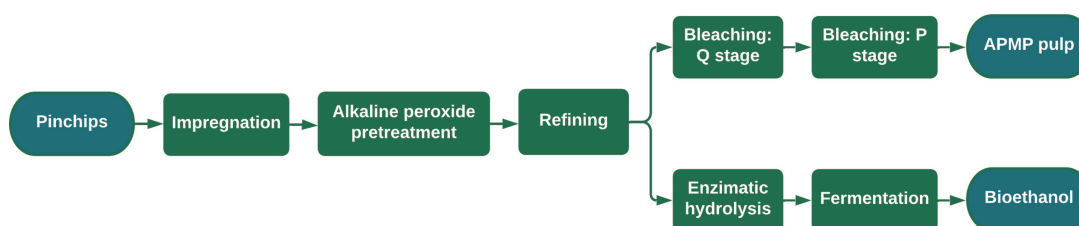


Figure 1.
Schematic description of the process.

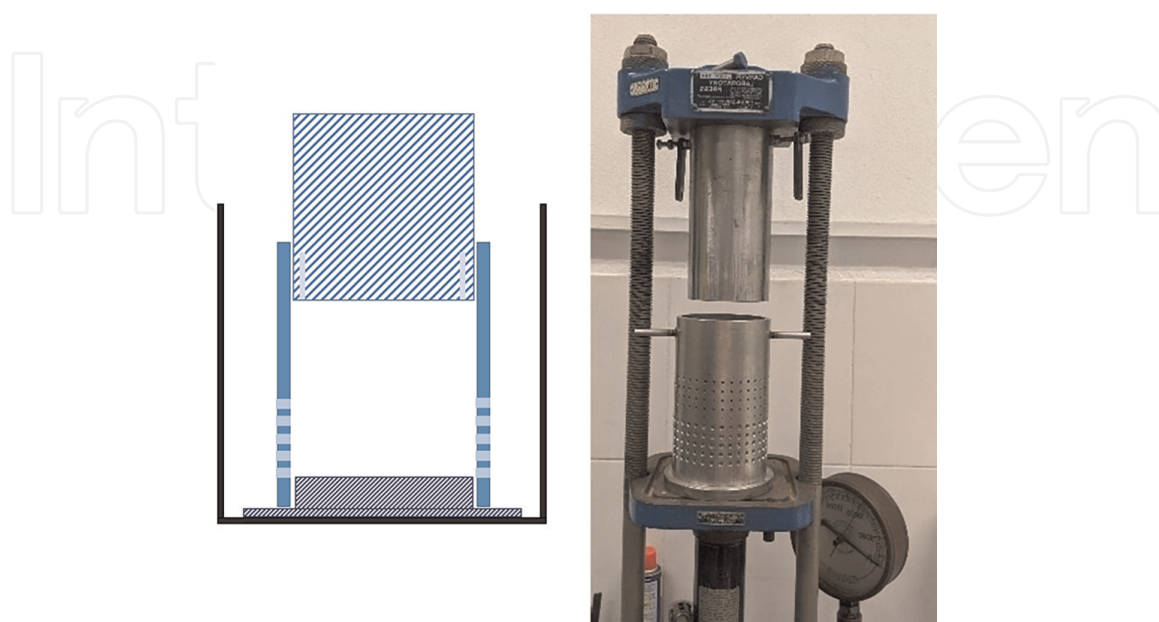


Figure 2.
Impregnator and press are used to remove the air inside the pin chips.

For pretreatment in the Parr reactor, preliminary trials were carried out following a factorial experimental design (Series A) using the following parameters: extraction temperature (50–100°C), time at that temperature (30–90 min), and doses of soda (8–12%) and peroxide (4–6%) used. In the design, a 2:1 (m:m) ratio of NaOH:H₂O₂ was applied. A constant level of 0.2% diethylenetriaminepentaacetic acid (DTPA) was used as a chelator. The function of DTPA is to remove heavy metals from the solution, particularly Mn²⁺, Cu²⁺, and Fe³⁺, to prevent the decomposition of H₂O₂. According to Kruzolek [16], the colored extractives present in eucalyptus also react with this chelating agent.

After the extraction, the material was drained and centrifuged at 1000 rpm, which separated the solid fraction from the liquid. The solid fraction was then extensively washed with deionized water until a colorless filtrate was obtained.

In the solid fraction, the extraction yield was determined by considering the initial dry mass and the dry mass obtained after extraction, which was later refined in a disc refiner to produce semi-chemical pulp or to increase the accessibility to the cellulose chains to favor enzymatic hydrolysis. Refining was performed in a disc refiner (Kumagai Riki Kogyo Co., Ltd., Tokyo, Japan) with 30-cm diameter discs and a gap of 0.1 mm. The net yield after refining was also determined.

Brightness was measured (ISO 2470-1:2016) in the refined pulp. The pulps with the highest net yield and brightness were characterized in terms of carbohydrate and lignin content according to the NREL TP-510-42,618 procedure. The liquid fraction (liquor) obtained after alkaline peroxide treatment was characterized in terms of pH and carbohydrates, lignin, and biomass degradation product content (acetic and formic acids, furfural, and hydroxymethylfurfural (HMF)) (NREL TP-510-42,623). Residual peroxide was measured by iodometry.

This experimental design was evaluated in terms of extraction yield, brightness after refining, and enzymatic hydrolysis efficiency.

With approximately 40% of the design completed, the yields obtained were extremely low, and the enzymatic hydrolysis efficiency was far from the expected value. Therefore, and in accordance with the bibliographic review focused on bioethanol production [29, 30], more exhaustive extraction conditions were used (Series B). For these assays, the NaOH:H₂O₂ ratio was adjusted to 1:1 (m:m). Initial tests were carried out at 75°C for 90 min in the pretreatment stage, varying the NaOH charge between 5% and 45%. For different soda charges (between 8% and 30%), the processing time was increased while maintaining the temperature at 75°C.

2.3 Pulp bleaching and papermaking properties

To produce cellulose pulp, the solids were bleached using a two-stage sequence: the chelating stage (Q) and the H₂O₂ stage (P). The purpose of the first stage was to remove metals to avoid the catalyzed decomposition of H₂O₂ [15]. This was performed at acidic pH, using EDTA as a chelating agent. The aim of the second stage was to oxidize chromophoric compounds derived from lignin fragments into colorless structures. The bleaching power of H₂O₂ is highest at a pH between 10 and 11. The Q stage was performed at 65°C for 60 min using charges of 0.4% EDTA and 0.8% sulfuric acid (initial pH = 3). The P stage was performed at 80°C for 150 min using charges of 0.3% NaOH, 0.375% H₂O₂, 0.02% magnesium sulfate, and 0.02% DTPA.

After bleaching, some pulps were selected based on the global yield and the final brightness obtained. The papermaking properties of these pulps were determined.

To determine the papermaking properties, pulps were refined using a PFI refiner at 4000 revolutions (ISO 5264-2). In refined and unrefined pulps, drainability in terms of Canadian standard freeness (TAPPI T227 om-17) was determined. Pulp sheets were then prepared and conditioned according to ISO standards (ISO 5264-2, ISO 5269-2, ISO 187). On those sheets, brightness, opacity (ISO 2471:1998), basis weight, tear and tensile index, and tensile energy absorption (TEA) were measured according to TAPPI T410 om-08, TAPPI T414-om86, and TAPPI T494-om04 standards, respectively.

2.4 Enzymatic hydrolysis

The refined pulps were enzymatic hydrolyzed to obtain a liquid fraction rich in glucose, to be fermented for bioethanol production. All assays were performed under the same enzymatic hydrolysis conditions. A commercial enzymatic complex (Cellic CTec 2 (Novozymes)) was used. Enzyme dosage was 15 FPU/g_{glucan} with a solid loading of 15% (w/w). The enzymatic hydrolysis was performed in Erlenmeyer flasks, pulps were suspended in a 0.05 M citric acid buffer solution (pH = 4.8) at 48°C for 96 h with orbital agitation at 150 rpm. Samples were taken at times 0 and 96 h. Tests were carried out by duplicate.

3. Results and discussion

3.1 Alkaline pretreatment

Figure 3 shows the aspects of the raw material, alkaline-treated solid, alkaline-extracted liquor, and refined pulp.

As expected, the solid obtained after pretreatment was brighter than the original raw material. This demonstrates the effect of H₂O₂. However, the liquor obtained presented a dark color, similar in visual appearance to that obtained in treatments without peroxide.

Table 2 shows the liquid and solid fraction results after pretreatment and refining assays (Series A).

The extraction yields for the alkaline peroxide pretreatment varied between 78.5% and 90.5%. However, no clear trend was observed within the parameters studied. These yields are comparable to those obtained by Liu et al. [31], who worked with aspen chips under similar conditions (temperature: 50–100°C, time: 10–60 min, soda

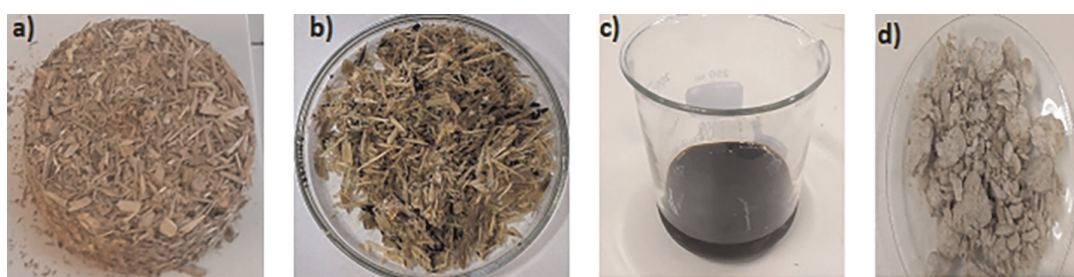


Figure 3.
a) *Eucalyptus pin* chips used as raw material; b) solid fraction after alkaline-peroxide treatment; c) liquid fraction obtained after alkaline-peroxide treatment; d) pulp obtained after mechanical refining process.

Condition applied				Solid fraction			Liquid fraction			
T (°C)	Time (min)	NaOH (%)	H ₂ O ₂ (%)	Extraction yield (%)	Yield after refining (%)	Brightness (% ISO)	pH	Lignin (%)	XS (%)	Acetyl groups (%)
50	30	10	5	90.5 ± 0.1	82.0 ± 0.1	49.7 ± 0.5	11.9	2.4 ± 0.1	0.7 ± 0.1	3.6 ± 0.1
50	30	8	4	85.1 ± 0.1	80.5 ± 0.1	48.3 ± 0.5	10.9	2.0 ± 0.1	n.d.	n.d.
50	60	8	4	89.5 ± 0.1	85.7 ± 0.1	50.2 ± 0.6	10.8	2.2 ± 0.1	0.5 ± 0.1	3.5 ± 0.1
50	90	12	5	86.6 ± 0.1	78.8 ± 0.1	48.6 ± 1.0	12.2	2.7 ± 0.1	0.9 ± 0.1	3.9 ± 0.1
50	90	8	4	87.8 ± 0.1	76.8 ± 0.1	53.4 ± 0.9	10.6	2.0 ± 0.1	0.5 ± 0.1	3.1 ± 0.1
75	30	10	5	90.2 ± 0.1	81.5 ± 0.1	n.d.	9.4	1.5 ± 0.1	n.d.	n.d.
75	30	8	4	78.4 ± 0.1	82.5 ± 0.1	48.8 ± 0.5	10.0	2.4 ± 0.1	0.5 ± 0.1	3.3 ± 0.1
75	60	8	4	85.1 ± 0.1	82.9 ± 0.1	50.2 ± 0.6	10.0	2.6 ± 0.1	0.7 ± 0.1	3.5 ± 0.1
75	60	10	5	78.5 ± 0.1	77.5 ± 0.1	48.9 ± 0.3	11.1	2.5 ± 0.2	0.2 ± 0.1	4.3 ± 0.1
75	90	8	4	89.1 ± 0.1	79.6 ± 0.1	49.5 ± 0.6	9.6	1.9 ± 0.1	0.3 ± 0.1	2.3 ± 0.1
75	90	10	5	87.5 ± 0.1	81.3 ± 0.1	47.6 ± 0.3	11.1	2.9 ± 0.2	0.8 ± 0.1	3.8 ± 0.1
100	60	12	6	86.5 ± 0.1	71.2 ± 0.1	50.9 ± 0.3	9.1	2.2 ± 0.1	n.d.	n.d.
100	90	10	5	86.8 ± 0.1	83.0 ± 0.1	46.7 ± 1.2	10.4	2.7 ± 0.2	1.0 ± 0.1	3.9 ± 0.1

Table 2. Solid and liquid fraction characteristics after alkaline pretreatment and mechanical refining of the Serie A assays. (XS: Xylosaccharides; n.d.: Not determined).

load 1.5%–6.7%, and NaOH:H₂O₂ ratio 2:1), obtaining extraction yields between 85% and 94%.

All liquors presented a pH higher than neutrality. The final pH of the liquors arose from the soda charge applied in each condition and the acetyl and/or uronic groups released during extraction, which partially neutralized the hydroxyl groups. Consequently, the highest pH in the liquor was achieved under low-severity pretreatment and a high soda charge.

Pulp brightness was between 46.7% and 53.4% ISO. The low variability detected among these values did not support the determination of a general trend. Kruzolek [16] reported brightness values in the range of 55.4–64.9% ISO when working with a smaller charge of soda but a higher NaOH:H₂O₂ ratio using *Eucalyptus grandis* chips. Moreover, Latibari et al. [32], when working with Paulownia wood at 70°C for 100 min and charges of NaOH and H₂O₂ between 1.5% and 5.0% each, reported an ISO brightness between 67.5%–69.0%. In this case, the highest value reached for brightness is explained by the fact that Paulownia wood has 12.1% of extractives in ethanol: acetone because these extractives are normally colored and easily removed in an alkaline medium during pretreatment before bleaching.

Regarding the liquid fraction, xylosaccharides (from the hemicellulose fraction in the raw material) and lignin content were too low to be used for producing value-added products.

The results obtained from the Series B assays are reported in **Table 3**.

When working at 75°C for 90 min, the extraction yield decreased linearly with the soda charge ($r^2 = 0.97$). Variations in the other parameters did not show a clear trend. Despite the large increase in the dose of soda and peroxide, the pulp's brightness hardly improved compared to the results obtained in Series A. Xylosaccharide content in the liquid fraction increased as much as 5.9%, which implies a removal of almost 40% of the Xylan present in the raw material. Li et al. [33] carried out a treatment using corn cobs with 50% H₂O₂ (pH 11.5) at 30°C for 24 h and extracted 56% of the initial hemicelluloses and 92% of the initial lignin. Gupta and Lee [34], when working at 60°C for 24 h with a soda and H₂O₂ charge of 50%, reported extraction of 40% of the xylosaccharides originally present in poplar wood. Hemicellulose extraction yields differ among authors and depend on the materials and conditions used. The latter tend to have longer reaction times, a high soda and peroxide charge, and low temperatures. The extracted xylosaccharides can be recovered by precipitation with ethanol and used for biofilm production [35, 36].

3.2 Pulp bleaching and papermaking properties

The bleaching procedure was applied to all pulps, and the nine pulps with the highest values of brightness and net yield were selected. These pulps were refined, and the papermaking properties of the refined and unrefined pulps were determined.

The mechanical and optical properties of the selected bleached pulps are shown in **Table 4**.

As can be expected, sheet density increased when the pulp was refined, making fibers more flexible and increasing the bonding capacity and the bonding area. Additionally, external fibrillation collaborates to increase interfiber bonding formation [15, 37]. The sheet density in this work was higher than the density reported in other studies working with eucalyptus chips [15, 16] or chips of other hardwood species [32]. The use of small wood increased the external fibrillation during refining, which

Conditions applied				Solid fraction			Liquid fraction			
T (°C)	Time (min)	NaOH (%)	H ₂ O ₂ (%)	Extraction yield (%)	Yield after refining (%)	Brightness (% ISO)	pH	Lignin (%)	XS (%)	Acetyl groups (%)
75	90	5	5	88.4 ± 0.1	78.4 ± 0.1	n.d.	8.9	1.5 ± 0.1	0.6 ± 0.1	3.2 ± 0.3
75	90	10	10	83.3 ± 0.1	78.7 ± 0.1	n.d.	11.3	2.4 ± 0.1	1.3 ± 0.1	3.1 ± 0.1
75	90	15	15	80.1 ± 0.1	51.2 ± 0.1	n.d.	12.8	2.5 ± 0.1	2.5 ± 0.1	3.4 ± 0.2
75	90	30	30	72.2 ± 0.1	66.8 ± 0.1	51.6 ± 0.5	12.7	3.2 ± 0.2	4.4 ± 0.2	3.5 ± 0.3
75	90	45	45	71.9 ± 0.1	61.2 ± 0.1	58.9 ± 0.9	12.5	3.9 ± 0.2	5.9 ± 0.2	3.5 ± 0.2
75	90	60	60	65.6 ± 0.1	53.7 ± 0.1	45.2 ± 0.4	12.3	4.3 ± 0.2	n.d.	3.5 ± 0.3
100	240	8	8	85.9 ± 0.1	56.3 ± 0.1	n.d.	6.9	2.4 ± 0.1	2.7 ± 0.3	3.2 ± 0.2
100	240	12	12	78.1 ± 0.1	67.0 ± 0.1	n.d.	9.6	2.8 ± 0.1	3.6 ± 0.3	3.6 ± 0.3
75	120	8	8	88.3 ± 0.1	58.8 ± 0.1	n.d.	7.4	1.8 ± 0.1	2.1 ± 0.1	3.5 ± 0.2
75	120	12	12	93.6 ± 0.1	48.6 ± 0.1	n.d.	10	2.6 ± 0.1	1.9 ± 0.1	3.5 ± 0.1
75	240	16	16	82.6 ± 0.1	66.6 ± 0.1	n.d.	12.8	2.6 ± 0.1	0.5 ± 0.1	3.9 ± 0.3

Table 3. Solid and liquid fraction characteristics after alkaline pretreatment and mechanical refining of the Serie B assays. (XS: Xylosaccharides; n.d.: Not determined).

T (°C)	Time (min)	NaOH (%)	H ₂ O ₂ (%)	Beating rev. (rpm)	CSF (mL)	Sheet density (kg/m ³)	Brightness (% ISO)	Opacity (%)	Tensile Index (Nm/g)	Tear Index (Nm ³ /g)	TEA (J/m ²)
50	60	8	4	0	349	405	64.5	93.6	15.9	1.9	0.08
				4000	107	546	63.7	93.2	30.2	1.8	1.1
50	90	8	4	0	200	452	73.3	89.6	23.9	2.18	0.2
				4000	76	595	72.5	90	37.5	2.04	0.34
75	30	8	4	0	302	453	75.6	86.3	24	2.32	0.2
				4000	72	609	75	86.9	42.7	2.3	0.46
75	90	30	30	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
				4000	57	786	74	78.5	42.6	1.44	0.34
75	90	45	45	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
				4000	37	777	73.8	77.5	41.6	1.2	0.31
75	120	8	8	0	340	455	73.5	84.1	25.5	2.86	0.21
				4000	81	623	72.9	84.5	47.2	2.93	0.72
75	240	16	16	0	339	526	72.6	83	35.6	3.57	0.36
				4000	79	681	71.1	82.4	60.0	3.36	0.88
100	60	12	6	0	529	410	76.2	82.7	15.5	2.41	0.08
				4000	120	624	75.4	84.6	46.8	2.87	0.55
100	90	10	5	0	300	518	70.4	86.9	35.3	3.23	0.43
				4000	91	654	69.2	86.2	52.4	3.26	0.74

Table 4.
Paper properties of selected bleached pulps at different degrees of refining.

increased the sheet density. Notably, the density increased with the chemical charge, producing more fibrillation and bulkier pulp.

Brightness improved after bleaching, but the brightness of the commercial pulps was generally higher. However, it is possible to obtain pulp with a higher final brightness when using a longer residence time in the P stage, carrying out this stage in two steps, or with higher chemical doses. Opacity was high for almost all bleached pulps, which is good for paper applications.

Tensile strength is useful in determining resistance to breakage. It is associated with the strength, length, and bonding of the fibers, which are also dependent on the degree of refinement. The tensile strength of the bleached pulps refined at 4000 rpm was high for all the conditions tested, reaching a tensile index of 60.0 Nm/g. The tear index for the refined pulps was also good, in accordance with the values reported by other authors [38–40].

Of the nine bleached pulps tested, two showed the best papermaking properties. The conditions for these pulps were as follows: (1) 75°C for 240 min with a dose of 16% soda and 16% peroxide and (2) 100°C for 90 min with a dose of 10% NaOH and 5% peroxide. The first pulp had slightly better properties. However, the increase in chemical loads and the high residence time did not justify the use of these conditions at the industrial level. In addition, the second treatment had a noticeably higher yield (83.3% vs. 66.6%), so a greater amount of pulp was obtained from the same amount of pin chips. Consequently, the conditions selected to scale up the process were 100°C for 90 min and a load of 10% NaOH and 5% peroxide.

3.3 Enzymatic hydrolysis

The chemical composition of the pretreated solids used and their behavior in enzymatic hydrolysis are listed in **Table 5**.

The solid pretreated with NaOH/H₂O₂ presented a maximum enzymatic hydrolysis efficiency of 23% when 10%, 12%, and 30% soda loads were used, and then its value decayed 1.5 times when 45% soda was used. By adding 6.25% H₂O₂, the efficiency increased from 30–40% and from 40–49% by the cellular structure alteration due to hemicellulose (49%) and lignin (26%) removal, which left the cellulose more accessible to the enzyme [41]. In this work, only slightly lower hydrolysis efficiencies (23%) were obtained by pretreating eucalyptus with NaOH (10)/H₂O₂ (5) at 75°C for 90 min, despite the fact that lignin removal was much lower (2.8%). Bagasse lignin is more easily solubilized with alkaline solutions due to the presence of lignin H (which contains p-hydroxyphenyl in its structure), which is not present in the wood [42]. Alvarez-Vasco and Zhang (2017) used different temperatures (25–180°C), reaction times (30–90 min), and H₂O₂ concentrations (4–10%) with spruce and observed that temperatures below 140°C were not effective in hydrolyzing cellulose (efficiency less than 25%) [43].

An increase in peroxide charge or reaction time worsened the enzymatic hydrolysis of the cellulose process. Several authors have reported low yields of enzymatic hydrolysis in lignocellulosic materials pretreated with the addition of alkalis, which can be attributed to the formation of pseudo-lignin or the solubilization of the amorphous fractions of cellulose, leaving more crystalline zones in the solid. Pseudolignin acts as a barrier, reducing the accessibility of the enzymes or retaining toxic compounds (furfural, HMF, phenolic compounds), making it difficult to remove them during washing [44–51].

Conditions applied				Solid composition (%)			Hydrolysis parameters at 96 h	
T (°C)	Time (min)	NaOH (%)	H ₂ O ₂ (%)	Glucan	Xylan	Lignin	Glucose (g/L)	Hydrolysis efficiency (%)
100	60	12	6	55.0 ± 0.8	12.0 ± 0.1	29.4 ± 4.4	14.1 ± 1.0	14.2 ± 1.0
75	90	5	5	51.4 ± 1.4	16.5 ± 0.5	26.5 ± 1.7	6.7 ± 0.3	5.2 ± 0.2
75	90	8	4	54.0 ± 1.3	12.2 ± 0.3	30.0 ± 3.9	9.7 ± 0.5	9.9 ± 0.1
75	90	10	5	55.8 ± 1.4	12.1 ± 0.2	32.5 ± 5.5	22.3 ± 1.0	23.3 ± 3.3
75	90	12	12	48.7 ± 3.6	18.4 ± 2.1	28.1 ± 0.1	21.4 ± 1.5	22.9 ± 2.8
75	90	30	30	51.0 ± 0.1	10.7 ± 0.0	30.2 ± 3.0	22.0 ± 0.5	23.3 ± 1.8
75	90	45	45	53.1 ± 0.4	9.4 ± 0.3	26.4 ± 0.2	15.5 ± 0.9	15.8 ± 0.7
75	90	60	60	54.9 ± 0.1	9.9 ± 4.0	29.5 ± 1.3	9.9 ± 1.3	10.5 ± 1.2
75	240	30	30	54.6 ± 0.3	14.9 ± 0.2	24.5 ± 4.0	14.5 ± 3.4	15.1 ± 3.4
75	480	30	30	47.6 ± 1.3	12.3 ± 0.1	26.5 ± 0.3	12.2 ± 1.2	14.3 ± 2.0

Table 5.
 Solids composition before enzymatic hydrolysis, glucose content, and hydrolysis efficiency.

The results obtained for the enzymatic hydrolysis of the alkaline peroxide-treated solids (based on the final concentration of glucose and enzymatic efficiency) were low. The low concentration of glucose obtained made it pointless to proceed with subsequent fermentation. Simultaneous hydrolysis and fermentation tests also had poor results (data not shown).

4. Techno-economic analysis

For the different processes, an economic analysis was carried out considering the annual profitability of each option. The revenues from product sales were equalized to the annual production costs (including the amortization of the investment), and the maximum price at which biomass could be purchased was calculated. This option was preferred to the classic analysis through the internal rate of return and the net present value because the investments required for the options listed below were quite different.

An economic comparison was performed for two options: (1) the installation of a power boiler plant to produce energy to be sold to the national grid and (2) the production of APMP to be sold to papermaking companies. To this end, the best conditions found in the experiment were used as working conditions. Due to the lower enzymatic hydrolysis efficiencies obtained, bioethanol production was not analyzed.

Both analyses were performed considering 50,000 dry tons/year of eucalyptus pin chips, with a water content of 45%, which corresponds with the number of pin chips generated for a modern kraft eucalyptus pulp mill with a capacity of 2.1 ADT¹/year. The prices used correspond to a plant located in Uruguay.

¹ ADT stands for Air Dry Ton and is commonly used in the pulp industry as a unit of measure for the pulp produced. It represents pulp with a moisture content of 10%; therefore, 1 ADT is equivalent to 0.9 ODT (Oven Dry Ton).

4.1 Techno-economic analysis for power generation alternative

To calculate the power boiler size (MW), Eq. (1) was used, considering a boiler efficiency of 85% and an efficiency in the vapor cycle of 25% (to convert steam to electricity) [52].

$$Biomassconsumption = \frac{Boilerpower}{Boilerefficiency * LHV} \quad (1)$$

A lower heating value of 11.3 MJ/kg was considered [53]. The values applied for the economic analysis are listed in **Table 6**.

Considering utilities equal to zero to calculate the maximum price of biomass and considering the energy selling price in the range of 50–70 MWh, different scenarios can be analyzed. The results are shown in **Table 7**.

In the first two cases, the price of biomass was quite low and probably would not cover the cost of biomass handling. However, for a scenario where the energy price reached 70 USD/MWh, which could be possible in Uruguay, the biomass price increased to 16.3 USD/ton, which is an attractive value.

4.2 Techno-economic analysis for an APMP mill

Considering the yields obtained in the experiment for a biomass availability of 50,000 ADT/year, the size of the APMP mill turn should be 41,500 ADT/year. The values applied for the economic analysis are listed in **Table 8** [52, 54].

Amortizable capital costs include yard improvements, machinery, equipment, buildings, utility services, and electrical and piping systems.

Investment (USD ²)	13.850.000
Operation	24 hours/330 days/year
Life of project	10 years
Installed kW cost ³	2700 USD/kWh
Connection to the national grid cost (USD)	350.000 USD [53]
Yard improvements	1% of fixed capital
Operation & Maintenance	4% of fixed capital

²USD means Dollar USA. ³Based on [53] and estimating the cost by scaling using the “six-tenths factor rule” [52].

Table 6.
Economic analysis parameters for power generation.

Energy sale price (USD/MWh)	Biomass maximum purchase price (USD/dry ton)
50	0.43
60	8.4
70	16.3

Table 7.
Result of economic analysis for power generation.

Investment (USD)		23,787,000
Operation		24 hours/330 days/year
Life of project		10 years
Variable costs	Operation and Maintenance	8% of fixed capital*
	Steam (USD)	2,746,000
	Power (USD)	3,846,000
	Chemicals (USD)	3,751,000

*Mechanical pulping is considered an aggressive process.

Table 8.
 Economic analysis parameters for APMP mill.

Pulp sale price (USD/ADT)	Biomass maximum purchase price (USD/dry ton)
350	15.2
400	58.2
500	144

Table 9.
 Result of economic analysis for APMP mill.

Considering utilities equal to zero to calculate the maximum price of biomass and considering the APMP selling price between 350 and 500 USD/ADT, different scenarios could be formulated. For this analysis, the recovery of chemical products or energy that would occur if the plant were related to a kraft mill was not considered. In this case, the profits would be even higher. The results are shown in **Table 9**.

Pulp production seems to be a more attractive business than energy production, although investments in both processes are quite different. However, if the selling price of the pulp falls to 332 USD/ADT, the cost of biomass at the mill gate becomes zero.

5. Conclusions

For the final disposal of massive waste generated by the forestry industry, three alternatives were proposed: the generation of energy through burning, the production of filler pulp for paper production, and the production of bioethanol.

According to the experimental results, the production of bioethanol was inhibited in the enzymatic hydrolysis stage, and a more detailed study is required to determine the causes. Thus, APMP pretreatment does not seem to be a viable option for bioethanol manufacturing.

The production of APMP from wood residues is possible and results in good-quality pulp. Therefore, the process can be considered by large kraft pulp production industries for the management of their wood residues.

The production of both power and APMP may be economically feasible. In both cases, the utility of the plant is extremely sensitive to the sale price of energy or pulp. In energy production, sales prices of USD 70/MWh are required, which is normally higher than the cost of wind energy but has been possible in some scenarios. In the

production of APMP, higher profits are obtained, but the profits depend strongly on the sale price, and a decrease to less than 332 USD/ADT makes the process unfeasible.

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Conflict of interest


The authors declare no conflict of interest.

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References

- [1] Korpinen R. On the Potential Utilisation of Sawdust and Wood Chip Screenings. Turku-Finland: Åbo Akademi University; 2010
- [2] Fujimoto S, Fukuda T, Kuroda M, Sasaki Y, Sakanishi K, Minowa T, et al. System efficiency and economical analysis of system for producing energy material from wooden biomass. *International Energy Journal*. 2006;7:289-298
- [3] Görgens JF, Carrier M, García-Aparicio MP. In: Seifert T, editor. *Bioenergy from Wood*. Vol. 26. Dordrecht: Springer Netherlands; 2014
- [4] Gerssen-Gondelach SJ, Saygin D, Wicke B, Patel MK, Faaij APC. Competing uses of biomass: Assessment and comparison of the performance of bio-based heat, power, fuels and materials. *Renewable and Sustainable Energy Reviews*. 2014;40:964-998
- [5] Integrated Pollution and Prevention Control. Best Available Techniques (BAT) Reference Document for the Production of Pulp, Paper and Board. 2015. Available from: https://eippcb.jrc.ec.europa.eu/sites/default/files/2019-11/PP_revised_BREF_2015.pdf
- [6] Bajpai P. Generation of waste in pulps and paper Mills. In: Bajpai P, editor. *Management of Pulp and Paper Mill Waste*. 1st ed. Springer: Cham; 2015. pp. 9-17
- [7] Widell H. Industrial-scale biomass combustion plants: Engineering issues and operation. In: Rosendahl L, editor. *Biomass Combustion Science, Technology and Engineering*. Woodhead Publishing Limited; 2013. pp. 225-277
- [8] Integrated Pollution Prevention and Control. Best Available Techniques (BAT) Reference Document for Large Combustion Plants - Industrial Emissions Directive 2010/75/EU [Internet]. 2017. Available from: <https://eippcb.jrc.ec.europa.eu/reference/> [Accessed: July 25, 2022]
- [9] Salomón M, Savola T, Martin A, Fogelholm CJ, Fransson T. Small-scale biomass CHP plants in Sweden and Finland. *Renewable and Sustainable Energy Reviews*. Elsevier Ltd. 2011;15:4451-4465
- [10] Carvalheiro F, Duarte LC, Gírio FM. Hemicellulose biorefineries: A review on biomass pretreatments. *Journal of Scientific & Industrial Research*. 2008; 67(November):849-864
- [11] Kim JS, Lee YY, Kim TH. A review on alkaline pretreatment technology for bioconversion of lignocellulosic biomass. *Bioresource Technology*. 2016; 199(2016):42-48. DOI: 10.1016/j.biortech.2015.08.085
- [12] Kumar AK, Sharma S. Recent updates on different methods of pretreatment of lignocellulosic feedstocks: A review. *Bioresources and Bioprocessing*. 2017;4(1):1-19
- [13] Zhao X, Zhang L, Liu D. Biomass recalcitrance. Part II: Fundamentals of different pre-treatments to increase the enzymatic digestibility of lignocellulose Xuebing. *Biofuels, Bioproducts and Biorefining*. 2012;6(5):561-579
- [14] Lehto JT, Alén RJ. Chemical pretreatments of wood chips prior to alkaline pulping - a review of pretreatment alternatives, chemical aspects of the resulting liquors, and pulping outcomes. *BioResources*. 2015; 10(4):8604-8656

- [15] MCS d M, Colodette JL, Jääskeläinen AS. Alkaline peroxide mechanical pulping of novel Brazilian eucalyptus hybrids. *BioResources*. 2012; 7(3):3823-3836
- [16] Kruzolek C. Aplicación de variantes del proceso de pulpado al peróxidoalcalino (APMP) a *Eucalyptus grandis* de 6 y 16 años. [Magíster en Madera, Celulosa y Papel]. Argentina: Universidad Nacional de Misiones; 2000
- [17] He W, Hu H, Li W. Multivariate-parameter optimization of the alkaline peroxide mechanical pulp (APMP) process for larch (*Larix gmelinii* Rupr.) using box-Behnken design. *Holzforschung*. 2013;67(7):727-734
- [18] Hu K, Ni Y, Zhou Y, Zou; Xuejun. Substitution of hardwood Kraft with aspen high-yield pulp in lightweight coated wood-free papers part I. synergy of basestock properties. *TAPPI Journal*. 2006;5:21-26
- [19] Hespell RB. Extraction and characterization of hemicellulose from the corn fiber produced by corn wet-milling processes. *Journal of Agricultural and Food Chemistry*. 1998;8561(97): 2615-2619
- [20] Ebringerova A, Heinze T, Ebringerová A, Heinze T. Xylan and xylan derivatives - biopolymers with valuable properties, 1: Naturally occurring xylans structures, isolation procedures and properties. *Macromolecular Rapid Communications*. 2000;21(9):542-556
- [21] Parajó JC, Alonso JL, Vázquez D. Effect of selected operational variables on the susceptibility of NaOH-pretreated pine wood to enzymatic hydrolysis: A mathematical approach. *Wood Science and Technology*. 1994;28(4):297-300
- [22] Park YC, Kim JS. Comparison of various alkaline pretreatment methods of lignocellulosic biomass. *Energy*. 2012; 47(1):31-35. DOI: 10.1016/j.energy.2012.08.010
- [23] Al-dajani WW, Tschirner U. Alkaline extraction of hemicelluloses from aspen chips and its impact on subsequent kraft pulping. In: *Engineering, Pulping & Environmental Conference*. Tappi; 2007
- [24] Lehto J, Alén R. Alkaline pre-treatment of hardwood chips prior to delignification. *Journal of Wood Chemistry and Technology*. 2013;33(2): 77-91
- [25] Svärd A, Brännvall E, Edlund U. Rapeseed straw as a renewable source of hemicelluloses: Extraction, characterization and film formation. *Carbohydrate Polymers*. 2015;133: 179-186. DOI: 10.1016/j.carbpol.2015.07.023
- [26] Svärd A, Moriana R, Brännvall E, Edlund U. Rapeseed straw biorefinery process. *ACS Sustainable Chemistry and Engineering*. 2019;7(1):790-801
- [27] Wang M, Li Z, Fang X, Wang L, Qu Y. Cellulolytic enzyme production and enzymatic hydrolysis for second-generation bioethanol production. *Adv Biochem Eng Biotechnol*. 2012;128:1-24
- [28] Yao M, Wang Z, Wu Z, Qi H. Evaluating kinetics of enzymatic saccharification of lignocellulose by fractal kinetic analysis. *Biotechnology and Bioprocess Engineering*. 2011;16(6): 1240-1247
- [29] Rabelo SC, Andrade RR, Maciel Filho R, Costa AC, Filho RM, Costa AC. Alkaline hydrogen peroxide pretreatment, enzymatic hydrolysis and fermentation of sugarcane bagasse to

- ethanol. *Fuel*. 2014;**136**:349-357.
DOI: 10.1016/j.fuel.2014.07.033
- [30] Dutra ED, Santos FA, Alencar BRA, Reis ALS, de Souza R, FR d, et al. Alkaline hydrogen peroxide pretreatment of lignocellulosic biomass: Status and perspectives. *Biomass Conversion and Biorefinery*. 2018;**8**(1): 225-234
- [31] Liu W, Yuan Z, Mao C, Hou Q, Li K. Removal of hemicelluloses by NaOH pre-extraction from aspen chips prior to mechanical pulping. *BioResources*. 2011;**6**(3):3469-3480
- [32] Latibari AJ, Pourali K, Roghani AF. Alkaline peroxide mechanical pulping of fast-growth paulownia wood. *BioResources*. 2012;**7**(1):265-274
- [33] Li J, Lu M, Guo X, Zhang H, Li Y, Han L. Insights into the improvement of alkaline hydrogen peroxide (AHP) pretreatment on the enzymatic hydrolysis of corn Stover: Chemical and microstructural analyses. *Bioresource Technology*. 2018;**265**(March):1-7.
DOI: 10.1016/j.biortech.2018.05.082
- [34] Gupta R, Lee YY. Pretreatment of corn Stover and hybrid poplar by sodium hydroxide and hydrogen peroxide. *Biotechnology Progress*. 2010;**26**(4): 1180-1186
- [35] Rochón E, Cabrera MN, Scutari V, Cagno M, Guibaud A, Martínez S, et al. Co-production of bioethanol and xylosaccharides from steam-exploded eucalyptus sawdust using high solid loads in enzymatic hydrolysis: Effect of alkaline impregnation. *Industrial Crops and Products*. 2022;**175**
- [36] Solier YN, Schnell CN, Cabrera MN, Zanuttini MÁ, Inalbon MC. Alkali-peroxide extraction of xylan from sugar cane bagasse. Characteristics and film forming capacity. *Industrial Crops and Products*. 2020;**145**(January):112056
- [37] Smook GA. *Handbook for Pulp and Paper Technologists*. 3rd ed. Atlanta, USA: Tappi Pr. 2003. p. 425
- [38] Area MC, Kruzolek C. Aplicación de variantes del proceso de pulpado al peróxido alcalino de *Eucalyptus grandis* de 6 y 15 años. In: Congreso Iberoamericano de Investigación en Celulosa y Papel Ciadicyp 2000. Puerto Iguazú. 2000
- [39] Felissia FE, Area MC. Pulpa mecánica al peróxido alcalino (apmp) de *Eucalyptus dunii*. In: XII Jornadas Técnicas de la Celulosa y el Papel, CONGRESO ATCP. Concepción, Chile: ATCP; 2007
- [40] Xu EC. Some of the latest investigations in P-RC APMP pulping of hardwood. Part 1: LCR at secondary refining. In: 88th PAPTAC Annual Meeting. Montreal: PAPTAC; 2002
- [41] Zhang H, Huang S, Wei W, Zhang J, Xie J. Investigation of alkaline hydrogen peroxide pretreatment and tween 80 to enhance enzymatic hydrolysis of sugarcane bagasse. *Biotechnology for Biofuels*. 2019;**12**(1):107
- [42] De Carvalho DM, De Queiroz JH, Colodette JL. Assessment of alkaline pretreatment for the production of bioethanol from eucalyptus, sugarcane bagasse and sugarcane straw. *Industrial Crops and Products*. 2016;**94**:932-941
- [43] Alvarez-Vasco C, Zhang X. Alkaline hydrogen peroxide (AHP) pretreatment of softwood: Enhanced enzymatic hydrolysability at low peroxide loadings. *Biomass and Bioenergy*. 2017;**96**:96-102
- [44] Bondesson PM, Dupuy A, Galbe M, Zacchi G. Optimizing ethanol and

methane production from steam-pretreated, phosphoric acid-impregnated corn Stover. *Applied Biochemistry and Biotechnology*. 2015; **175**(3):1371-1388

[45] Hu F, Jung S, Ragauskas A. Pseudo-lignin formation and its impact on enzymatic hydrolysis. *Bioresource Technology*. 2012; **117**:7-12

[46] Kumar R, Hu F, Sannigrahi P, Jung S, Ragauskas AJ, Wyman CE. Carbohydrate derived-pseudo-lignin can retard cellulose biological conversion. *Biotechnology and Bioengineering*. 2013; **110**(3):737-753

[47] Leskinen T, Kelley SS, Argyropoulos DS. E-beam irradiation & steam explosion as biomass pretreatment, and the complex role of lignin in substrate recalcitrance. *Biomass and Bioenergy*. 2017; **103**:21-28

[48] Rigual V, Santos TM, Domínguez JC, Alonso MV, Oliet M, Rodriguez F. Combining autohydrolysis and ionic liquid microwave treatment to enhance enzymatic hydrolysis of Eucalyptus globulus wood. *Bioresource Technology*. 2018; **251**:197-203

[49] Sannigrahi P, Kim DH, Jung S, Ragauskas A. Pseudo-lignin and pretreatment chemistry. *Energy & Environmental Science*. 2011; **4**(4): 1306-1310

[50] Sun S, Cao X, Sun S, Xu F, Song X, Sun RC, et al. Improving the enzymatic hydrolysis of thermo-mechanical fiber from Eucalyptus urophylla by a combination of hydrothermal pretreatment and alkali fractionation. *Biotechnology for Biofuels*. 2014; **7**(1):116

[51] Pönni R, Galvis L, Vuorinen T. Changes in accessibility of cellulose during Kraft pulping of wood in

deuterium oxide. *Carbohydrate Polymers*. 2014; **101**:792-797

[52] Peters M, Timmerhaus K, West R. *Plant Design and Economics for Chemical Engineers*. 5th ed. McGraw-Hill Education; 2002 1008 p

[53] De Garcia Soria X, Villasante C, Cabrera C. *Evaluación Económico – Financiera- Proyecto 10 MW Generación de Electricidad a partir de Residuos y/o Subproductos de Biomasa*. Montevideo-Uruguay; 2008

[54] Cabrera M, Cocchiararo F, Figares M, Giradello S, Palombo V. *Diseño de una planta de fabricación de celulosa CTMP*. Montevideo: Facultad de Ingeniería, Universidad de la República; 2018