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Abstract

The present work proposes a cascading approach to fractionate thermally treated wood after life service and untreated wood and their unweathered counterparts. The fractioning of wood was implemented, focusing on the current trends in environmentally friendly processing and processes with a noteworthy yield and purity. Resulting streams: cellulose, hemicelluloses, and lignin. These fractions were analyzed utilizing spectroscopies (ultraviolet and infrared), chromatography (liquid and gas), thermogravimetry, and x-ray diffraction (thermal treatment and weathering). Results showed no significant difference in yielding or the quality of the extracted celluloses (only a slight increment of the crystallinity after the thermal treatment). Considering the hemicellulose fraction, it was observed a considerable mannose reduction after the thermal treatment (≈37%) and weathering (≈27%), or the combination of both (≈51%). Nevertheless, the most notable changes were observed in the yield and the quality of the obtained lignins with higher yields for untreated wood (Po) and more purity (>93%) for lignin samples obtained during the delignification process (L1). Their structure was also affected by the fraction from which they were extracted, as reflected by the S/G ratio. Moreover, the thermal and weathering treatment improved their thermal properties, as shown by thermogravimetric analysis. In general, the present work proved the feasibility of valorizing thermally treated wood after service life within a biorefinery system to obtain competitive value-added products to optimize resources and extend the utility time of such biomass.

Keywords: heat-treatment, organosolv lignin, cellulose, wood products, fractionation, cascade approach

1. Introduction

The use of wood-based products in Europe is projected to increase threefold worldwide between 2010 and 2050 (Dammer et al., 2016). In this frame, the inventories of Monterey pine (*Pinus radiata* D. Don) in the Basque Country, where is located this research work, has reported an increase in wood production from 15 million m^3 in 1976 to more than 27 million m^3 in 2017 (Etxabe Villasante, 2018). This fact has awakened considerable interest in using this vital resource in high value-added applications after its modification, such as building applications after its thermal or chemical treatment, elaboration of biomaterials, plywood, fiberboards, among others (Wei et al., 2019). Monterey pine is the species that occupy the most significant area (31 % of the total wooden forest area) and about 85-90 % greater forest productivity in the Basque Country. Basque forests can be considered one of the lands with the highest concentrations of Monterey pine in the northern hemisphere; it should be regarded as an essential asset for the local economy (Cantero, 2014). However, the highly fractioned size of private-owned forestlands, the aging of the local population and the strong regulations to cut down have supposed a challenge to the exploitation of pine by the local owners, which often cut down the trees, then leave them as green timber. In this sense, a proficient value-added application has been installing a kiln by local entrepreneurs, who have developed a thermal modification process marketed as Thermogenik®. This method has treated local wood samples for outdoor applications such as roofing, decking, and façades. The performance of thermally modified woods has been deeply studied for several applications, showing outstanding results(Herrera et al., 2018). However, in the frame of demands and projections of the XXI century, the mere upgrading of wood or timber as a material is not enough.

The thermal modification of wood is an industrial process that take place at temperatures between 170-220 °C in a reduced oxygen atmosphere (e.g. steam saturated, gas, oil) in order to prevent oxidative combustion of the

wood components. The thermally modified wood (TMW) presents better dimensional stability, hydrophobicity, and protection against rot fungi (Jones and Sandberg, 2020). The most notable characteristic of the TMW is its color change to darker tones, and durability, which can considerably improve the wood durability class depending on the type of wood and the treatment conditions. The changes in the wood during thermal modification were studied in last decades and several patents and parent were developed. According to the European Committee for Standardization (European Committee for Standardization, 2008) TMW is wood in which the composition of the cell-wall material and its physical properties have been modified by exposure to a temperature higher than 160 °C with limited access to oxygen. The main changes in the wood matrix are the redistribution of lignin components, the degradation of hemicelluloses caused by deacetylation and the acid catalyzed hydrolysis of the polysaccharide chains, cross-linking and repolymerization reactions with different characteristics depending on the species, atmosphere, and temperature(Herrera-Díaz et al., 2019; Jones and Sandberg, 2020; Li et al., 2017).

The assessment of the process-related environmental impact of heat treatments has been limited; this can be because they lack chemicals and have encouraged the assumption that heat treatments are intrinsically more eco-friendly. According to Sandberg and Kutnar, TMW materials can mitigate climate change and promote sustainable development by reducing energy intake, solid and volatile emissions, reducing pollution, and ecosystem damage (Sandberg and Kutnar, 2016). Despite the industrial expansion of heat treatments, environmental guidelines are becoming more restrictive, and there is an increase in the sensitivity and awareness of the market to the environmental performance of products and services, preferring those that are eco-friendly.

At the present stage, it is necessary to consider the environmental performance of the thermally modified products and end-of-life scenarios to create strategies after the end of life of products. In general, to develop an environmental performance of a product is necessary to include recycling, upcycling, the cradle-to-cradle/cradle-to-gate paradigm, and end-of-life disposal options. Several studies on ecological solutions in the process stage are performed, mainly focused on releasing volatile compounds into the atmosphere, including recovery by condensation, purification, and successive filtration processes (Herrera et al., 2016a).

Additionally, the post-service-life reuse or disposal of any material requires strict handling, even for a bio-based material as wood. For this reason, several European countries have developed facilities for the energetic valorization of bio-based materials after their usage (Bentsen and Felby, 2012). Nevertheless, the life cycle assessment of wood as a material is truncated if energetic valorization is the following step after service life (Campbell-Johnston et al., 2020). Instead, the fractionation of the lignocellulosic macro components that constitute wood: holocellulose and lignin carbohydrate and aromatic fractions could open a frame to increase the value and service of wood after its first use, following the principles requested by the circular economy concept, which are considerably demanding nowadays (Islam et al., 2020). In this sense, the cascading approach is considered the most suitable method for the whole valorization of the different biomass fractions. There are three definitions of cascading processes: cascading-in-time, cascading-in-value, and cascading-in-function. Cascading in function has been described as a process through which different products can be produced simultaneously, maximizing the value of the original biomass, resembling the functionality of a biorefinery (Keegan et al., 2013; Olsson et al., 2016; Sokka et al., 2015).

The most common process to fractionate the wood-based materials is the one applied for the pulp and paper industry, namely, the Kraft process, followed by an elemental chlorine-free (ECF) sequence to bleach the intermediate pulp. However, more environmentally friendly processes can be designed, such as sulfur-free pulping processes or total chlorine-free bleaching sequences (TCF) (Oliaei et al., 2020; Robles et al., 2018). Concerning the pulping stage, the organosolv delignification process includes a diverse range of organic solvents to fractionate lignocellulosic biomass into rich cellulose pulp, a water-soluble hemicellulose stream, and a concentrated lignin fraction. The organic solvents triggered the solubilization of lignin without altering its chemical structure to a high degree, which has positioned these processes into the most attractive ones to

preserve the native structure of lignin during the extraction without undergoing strong recondensation reactions (Pandey and Kim, 2011). The high purity of the obtained lignin by these methods, together with the lack of sulfur in its molecular structure, allows lignin to be employed as a source of aromatic structures to produce high added-value chemicals, which can be used for the production of adhesives, binders, in polymer substitutions or as a phenolic precursor (Zakzeski et al., 2010; Zhao et al., 2017). Besides, the low boiling point of the organic solvents allows the recovery of the solvent to avoid its disposal after the process (Fernández-Rodríguez et al., 2020). Thanks to all these advantages, it is expected that the organosolv methods may awaken more industrial interest in the future for biomass fractionation (da Silva et al., 2019).

For the bleaching stages, the TCF sequences constitute environmentally friendly alternatives to remove the phenolic chromophores from the remaining lignin fraction in the cellulosic pulp without chlorine compounds due to their adverse environmental effects (Ibarra et al., 2006; Nelson, 1998). When doing a TCF bleaching, removing the metals becomes more critical because hydrogen peroxide is applied early in the sequence at higher charges. The elimination of the metals is improved with the addition of a chelating agent. Ethylenediaminetetracetic acid (EDTA) and diethyleneaminepentacetic acid (DTPA) compounds are the best chelating agents for double-charged metal ions. However, using either DTPA or EDTA in "green pulping and bleaching" is currently discouraged as none of these agents is biodegradable, nor are they efficiently handled, as standard water treatment plants cannot remove these components from water. Therefore, they represent considerable harm to the ecosystems in which those streams are deployed. For this reason, it is recommended to use another metal chelating agent, such as the 2,6-Pyridinedicarboxylic acid (PDA), which has been proved to be an effective chelating agent with similar results to those of EDTA (Pinto et al., 2015).

In the present work, the cascading of local wood residues after its usage to be transformed into bio-based materials by fractionating the whole structure of the macro-components is approached. The goal is to guarantee the integral valorization of these residues by obtaining building block components capable of being transformed into high-value-added compounds. An environmentally friendly and robust process has been designed using an organic acid pretreatment, a sulfur-free delignification stage, followed by a TCF bleaching sequence. This allowed obtaining cellulosic pulp, hemicelluloses, and lignin as main compounds with innovative green processes.

2. Material and methods

2.1. Materials

Monterey pine (*Pinus radiata D. Don*) was obtained from the forest areas of the Basque Country (Spain). Wood was debarked, sawed, stored, and conditioned before the heat-treatment at Torresar® Company in fulfillment of the chain of custody according to the PEFC certification. The boards of Pinus radiata were principally from heartwood with the annular rings at 30 degrees to the face of the board (tangential grain). The load of Pinus radiata was modified in an industrial chamber according to industrial production standards at 212 °C (Bruno M. Esteves et al., 2020) under a saturated steam atmosphere for 60 h (Termogenik®, Spain). The modification process begins with a rapid increase of the temperature to 100 °C, allowing the drying of the wood to 3–4% of moisture content. Subsequently, steam is sprinkled to avoid wood damage, and the temperature in the chamber is raised to its maximum temperature (212 °C). The last stage is the cooling down and stabilizing of the samples. This stage takes about 24 h, at controlled relative humidity until room temperature to avoid abrupt temperature and pressure fluctuations (Herrera et al., 2016b).

A set of samples (20 dried wood and 20 thermally modified wood) with the dimensions of 9 x 170 x 170 mm were exposed twelve months to natural weathering in wooden support at 45 degrees of inclination and facing south direction (from May to April) in a location with oceanic climate (San Sebastian, Spain: 43°18'33.054" Latitude N; 2°0'34.817" Length W). Subsequently, weathered samples were conditioned at 20 °C and 65% RH before analysis reported previously (Bruno M. Esteves et al., 2020). Samples of dry Monterey pine (Po), weathered dry pine (Pw), thermally treated pine (To), and weathered thermally treated pine (Tw) were

statistically selected to compare the influence of the weathering process on the lignocellulosic components of pine and thermally treated pine. In detail, a multiple comparison procedure analysis of variance (ANOVA) was used to determine which means were significantly different from others, and the confidence levels were examined. Bonferroni Significant Difference (BSD) was applied after rejecting the null hypothesis. The software used for this statistical and graphing analysis was OriginPro 9.7.0.185.

2.2. Fractionation processes

The stages of the fractioning were selected to develop a globally environmentally friendly process to leverage all the lignocellulosic platforms as different biomaterials from this forestry product after the end-life, as reported by this group (Fernández-Rodríguez et al., 2017b; Robles et al., 2018). For this purpose, acid pretreatment, organosolv treatment, and totally chlorine-free bleaching were selected. These stages constitute a sustainable process, focusing on the low environmental impact of the chemicals used through all the involved steps. All the reactions were carried out in a 4 L Zipperclave (Autoclave Engineers, Division of Snap-tite, Inc.) with PC-controlled stirring, pressure, and temperature. The global flowsheet of the followed process and the description of the obtained samples are detailed in Figure 1.

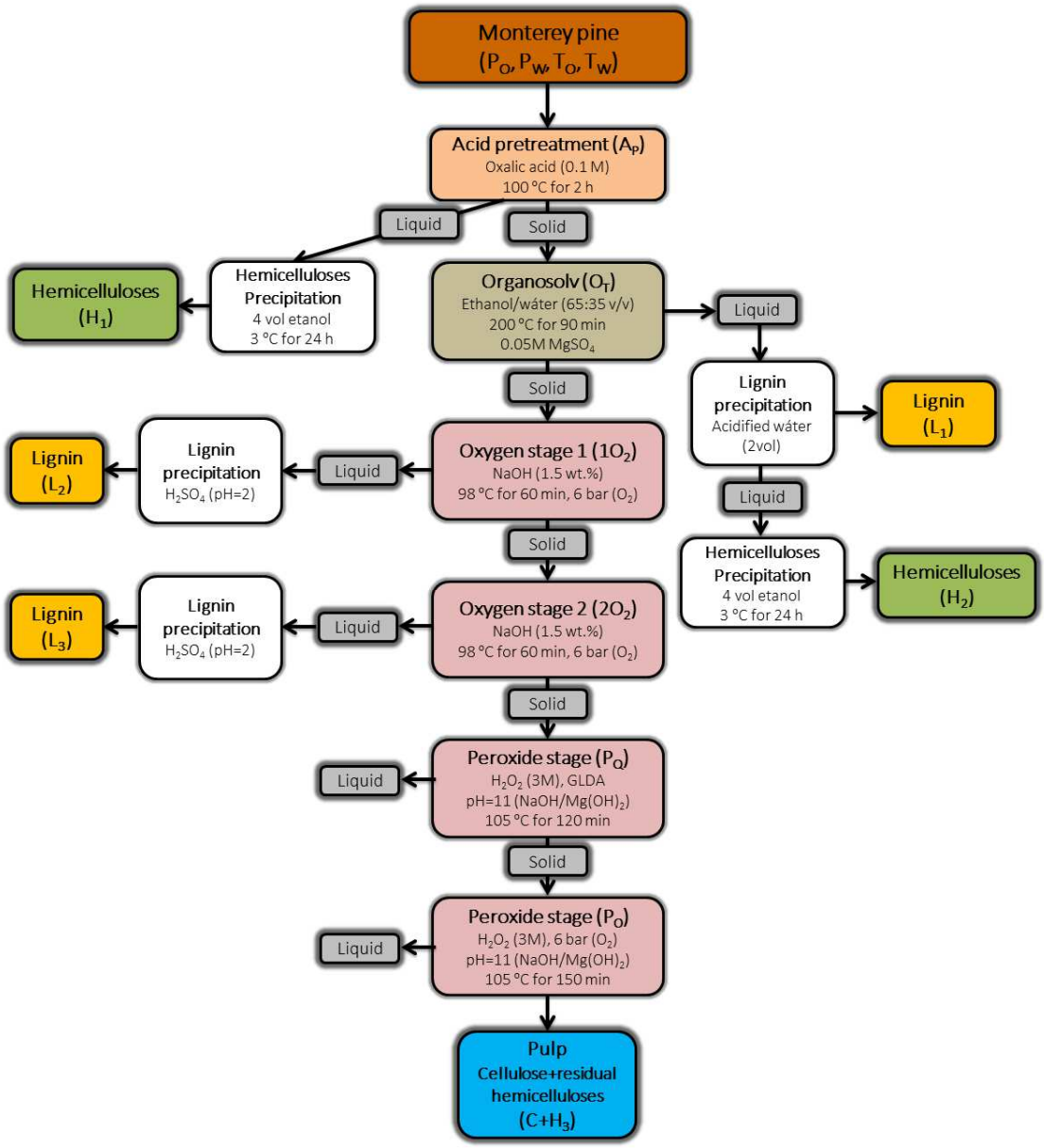

Figure 1. Flowsheet of the process and the recovered fractions.

2.1.2. *Acid pretreatment (A_P)*

All samples were chipped to an average of 10 mm chips and washed with a 0.1 M oxalic acid solution for 2 h at 100 °C (Barana et al., 2016). Hemicelluloses were precipitated from the liquid fraction with 4 volumes of ethanol at 3 °C for 24 h (Reyes et al., 2013), after which the solid precipitate was separated by centrifuging the suspension and washing the pellet until neutral pH was achieved; ethanol used in this stage was recovered via rotary evaporation and used for the following stage. The recovered solid fraction was called H1; an aliquot of the liquid after centrifuging was kept to analyze non-precipitated sugars.

2.1.3. *Organosolv delignification (O_T)*

The organosolv process was conducted using a mixture of ethanol/water (65:35 v/v) as a solvent, at 200 °C for 90 min and fiber to liquid ratio of 1:10 (w/v), adding 0.05M $MgSO_4$ as catalyst (Nitsos et al., 2018). The liquid

fraction was separated via filtration, and the solid fraction was washed several times until driving the remaining fibers to a neutral pH. Lignin (L_1) was precipitated from the spent liquor by adding two volumes of acidified water (pH = 2), after which the solid fraction was filtered with a 0.22 µm membrane. Hemicelluloses that could be extracted during this process were isolated by the remaining filtrate concentration, adding 4 volumes of ethanol, and kept at 3 °C for 24 h; afterward, the solid precipitate (H2) was isolated by centrifugation.

2.1.4. Bleaching sequence

The Totally Chlorine Free Bleaching sequence was designed to purify the fibers obtained during the delignification stage. This sequence was based on two alkaline oxygen stages ($1O_2$ & $2O_2$); one stage hydrogen peroxide with a secondary chelating reaction (P_Q) and the final one with alkaline peroxide under oxygen atmosphere (P_O). Oxygen-alkaline stages ($1O_2$ & $2O_2$) were equally carried out with 1.5 wt% NaOH for 60 min at 98 °C, and the pressure of the autoclave was maintained at 6 bar using O_2 atmosphere (Ibarra et al., 2006). The liquid waste fractions from these stages were collected to precipitate lignin by their acidification using H_2SO_4 (96 wt%) until pH = 2. In this sense, two more lignin fractions were obtained (L_2 and L_3). The first stage with hydrogen peroxide was done using 3M H_2O_2, at pH=11, stabilized with a mixture of NaOH and $Mg(OH)_2$ (3:1 wt%). The use of $Mg(OH)_2$ as a partial substituent of NaOH was effectuated as it has been reported its efficiency as an alkaline agent for peroxide bleaching with a 30% substitution being the optimal(Kong et al., 2009). The reaction was performed for 120 min at 105 °C with N, N-bis(carboxymethyl)glutamic acid (GLDA, CAS: 58976-65-1) as a chelating agent. GLDA constitutes an environmentally friendly substitution of the traditional chelating agents, such as EDTA or DTPA, which are difficult to be eliminated from water effluents(Koodynska, 2011). The final stage was performed using at 105 °C for 150 min; the reaction was kept under constant pressure of 6 bar of an O_2 atmosphere (Robles et al., 2018). In this stage, a 3M H_2O_2 was used, the pH was stabilized at pH=11 with NaOH, without any chelating agent. For all the reactions, the liquid to solid ratio was 10:1 (w/v).

2.2. Analytical methods

The initial characterization of the raw material was carried out according to standard methods developed by the Technical Association of the Pulp and Paper Industry (TAPPI): moisture (TAPPI T 264 cm-07, 2007), inorganic content (TAPPI T 211 om-16, 2016), ethanol-toluene extractives (TAPPI T 204 cm-07, 2007) Klason lignin (TAPPI T 222 om-11, 2011), holocellulose(Wise et al., 1946), cellulose, and hemicelluloses(Pettersen, 1984) were quantified. Scanning electron microscopy images were obtained with a Scanning electron microscope JEOL JSM-6400 F with field emission cathode and a lateral resolution of 10-11 Å at 20 kV. Samples were analyzed by Fourier Transform Infrared Spectroscopy (FT-IR) with a PerkinElmer Spectrum Two Spectrometer, equipped with a universal Attenuated Total Reflectance (ATR) accessory with an internal reflection diamond lens. The defined range of wavelength was from 4000 to 400 cm^{-1} and the resolution 4 cm^{-1}. For each sample, 30 scans were recorded.

The cellulose fraction was analyzed by X-ray diffraction with a Panalytical Phillips X'Pert PRO multipurpose diffractometer. Samples were mounted on a zero background silicon wafer fixed in a generic sample holder, using monochromatic CuKα radiation (λ = 1.5418 Å) in a 2θ range from 5 to 50 with a step size of 0.026 and 80 s per step at room temperature. The NMR spectrometry for ^{13}C was performed using a Bruker 500 MHz spectrometer (Billerica, MA, USA) at 250 MHz of frequency at room temperature. The spectrum was recorded with cross-polarization and magic-angle spinning.

The samples from the stages where the hemicelluloses were precipitated, namely H1 and H2, were analyzed via high-performance liquid chromatography (HPLC). This analysis was performed using a Jasco LC Net II/ADC chromatograph equipped with a refractive index detector and a diode array detector to determine the concentration of the main monomeric sugars (glucose, xylose, arabinose, and mannose) and degradation products (acetic acid and formic acid). These compounds were analyzed using a column Phenomenex Rezex ROA. The mobile phase was a solution of 0.005N H_2SO_4 with a flow rate of 0.35 mL min^{-1} and a column temperature of 40 °C. For this analysis, the solid samples of H1 and H2 were previously dissolved in acidified

water, and then they were filtered through membranes of 0.22 µm pore size. For the quantification of the main monomeric sugars and degradation products, standards of high purity and a known concentration of D-(+)-glucose, D-(+)-xylose, D-(-)-arabinose, and D-(+)-mannose, acetic acid glacial and formic acid were employed.

Lignin was evaluated in terms of purity and composition, measuring the Acid Insoluble Lignin (AIL), as well as Acid Soluble Lignin (ASL) following standard methods for quantifying the purity of sulfur-free lignin samples (TAPPI T 222 om-11, 2011; TAPPI T 249 cm-09, 2009). Carbohydrates extracted during the AIL method were also determined by High-Performance Liquid Chromatography (HPLC), following the same method described above.

The molecular weight average (M_w) and polydispersity index (M_w M_n^{-1}) were measured by Gel Permeation Chromatography (GPC) using a Jasco LC-Net II/ADC device, equipped with a reflex index detector, PolarGel-M column (300 mm, 7.5 mm), and PolarGel-M guard (50 mm 7.5 mm). Samples were prepared in dimethylformamide with 0.1 % lithium bromide as a mobile phase, injected using a 0.7 mL min^{-1} flow at 40 °C. The calibration was carried out using polystyrene standards ranging from 266 to 70,000 g mol^{-1}.

In addition, lignin samples were characterized by pyrolysis–gas chromatography-mass spectroscopy (Py–GC–MS), where each sample was thermally degraded in an inert atmosphere, after which its macromolecules break down at specific lower bonding energy points, forming volatile fragments that provide useful structural information about lignin as a whole. The Py–GC–MS was carried out following the method described by this group using a commercial pyrolyzer (Pyroprobe model 5150, CDS Analytical Inc., Oxford, PA) (Herrera et al., 2014). A Thermogravimetric Analysis (TGA) was also carried out to determine the thermal transitions and the thermal stability of the lignins. This characterization was carried out in a TA Q2500 calorimeter, with a 10 °C min^{-1} heating ramp, from 30 to 800 °C under an N_2 atmosphere.

3.1. Results and discussion

3.1 Feedstock characterization

As the first step, it is shown in Figure 2 the characterization of the different feedstock used in this work. As it can be seen, during the weathering of the non-thermally treated material (Pw vs. Po), the percentages of the carbohydrate macrocomponents (celluloses and hemicelluloses) were reduced, whereas the portion of lignin increased, showing in all cases a significant difference at the $p<0.05$ level. This involves the weathering affected mainly the polysaccharides that are easier to be degraded (hemicelluloses and the amorphous cellulose section). On the contrary, it was more difficult to degrade the aromatic lignin structures, which led to an increase in the lignin percentage in Pw. The use of the thermally treated sample (To vs. Po) provoked the same effect as the weathering, but more intense, with a higher decrease of the percentage of carbohydrates (especially hemicellulose, which showed a significant reduction at the $p<0.05$ level) and the corresponding increase of the lignin fraction. This was caused by the solubilization of the hemicelluloses and the small amorphous portion of the cellulose, remaining the lignin in a bigger concentration due to its stabilization by the polycondensation reactions of lignin undergone during the thermal treatment, as reported by Herrera and collaborators (Herrera et al., 2016a). However, a trend change was experienced when the weathering was applied over a thermally treated material (To) since the carbohydrate platform increased in percentage of the remaining material after the weathering. At the same time, the lignin content was decreased, in the opposite tendency as in Pw. The reason is based on the influence of the thermal pretreatment, as during this step, the carbohydrate composition that was more prone to be extracted was already solubilized, this resulted in no significant differences ($p<0.05$) between the lignin content of Pw and Tw. In this sense, the portion of carbohydrates still in the feedstock was more recalcitrant to be degraded by the exposure to the environment. Therefore, the removal of some carbohydrates during the thermal pretreatment led to generating a substrate more resistance and steady during the weathering exposure, as the weaker parts of the carbohydrate platform were already extracted, which can be considered a strong advantage of the thermal treatment. Nevertheless, the lignin composition increase led to higher availability, comparing To against Po, to be attacked by the weather conditions, since lignin is a sensitive component to be photo-degraded by weathering (George et al., 2005).

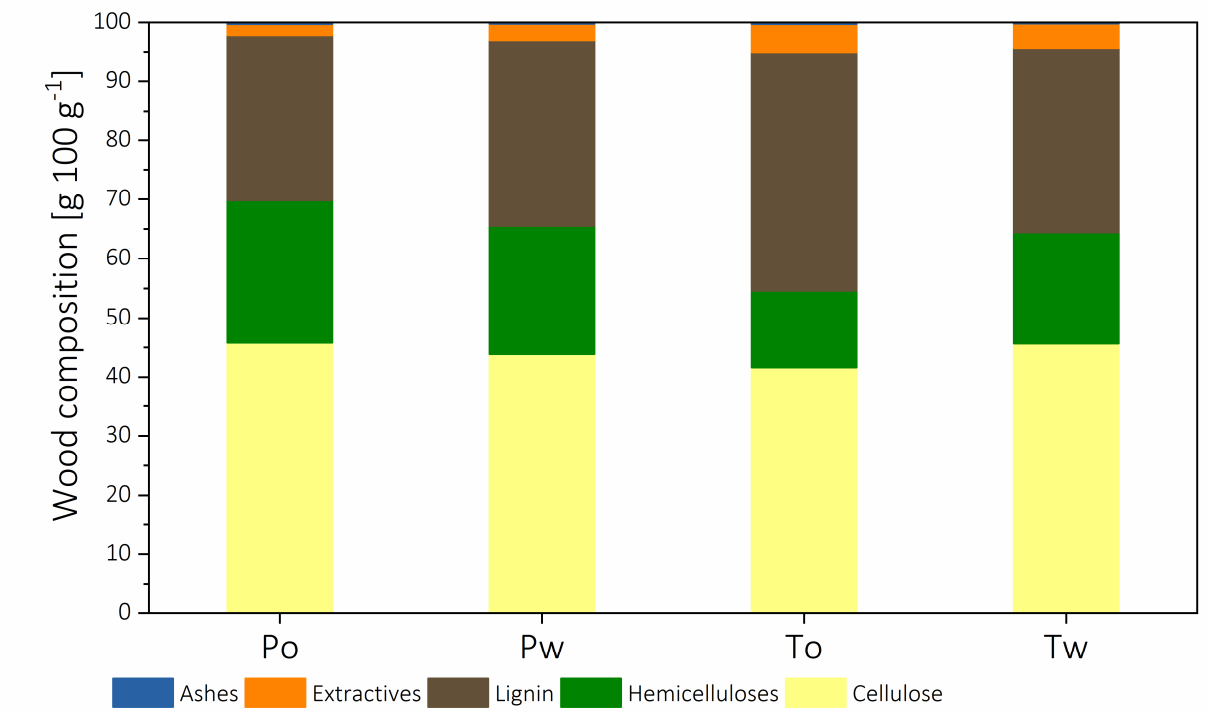

Figure 2. Chemical composition of the used biomass (Po: Monterey pine; Pw: weathered pine; To: treated pine; Tw: weathered thermally treated pine), further information is presented in Table S7.

3.2. Fractionation yields

The relative extraction yields for each recovered fraction (cellulose, lignin, and hemicelluloses) were presented in Figure 3. Tables S1 to S6 present additional information concerning the recovered fractions after each process.

The extraction yield of cellulose (C1), expressed as the cellulose content of the pulp obtained after the whole process, showed similar yields for the materials that were not thermally treated (Po and Pw). However, there was a decrease in the cellulose yield in the case of To (45.46%). Therefore, the thermal treatment provoked a decrease in cellulose in the initial material, as shown in Figure 2. This different behavior of To was not experienced by Tw, as the extraction yield (61.11%) was closer to the Ry of Po (65.9%) and Pw (64.07%). Thus, in this case, the weathering mitigated the influence of the thermal treatment.

From the lignin yields, it can be established that the process to extract lignin by this route was adequately designed as it allowed almost a total Ry for the Po, with a total lignin extraction (L1+L2+L3) of around 98.62%. However, when the initial material was subjected to thermal treatment or a weathering period, the extraction of lignin in the O_T stage was deeply impacted, with a reduction of L1 from ≈65% in Po to 30-40% for the other feedstock. Regarding the yields from different stages, the main extraction occurred during the organosolv process (L1) as was expected, especially in non-thermally treated pine (Po and Pw). Although the L1 samples from the thermo-treated wood (To and Tw) showed lower extraction yields for L1, the yields for L2 (31.15% and 24.33%, respectively) were similar to L2 extraction yields for Po and Pw (31.35% and 13.18%). The reason can be based on the new nature of the remaining lignin or para-lignin after the thermal treatment, as reported before (Herrera et al., 2014), where it was pointed out that the original lignin undergoes several reactions of polycondensation above 190 °C. These reactions are caused by the initial demethoxylation of the methoxy groups of guaiacyl and syringyl units that allowed free ortho sites in the aromatic rings to be cross-linked with other components fragments of cellulose and hemicelluloses when the temperature was above 190 °C. This more condensed structure is less sensitive to be extracted by the solubilisation with organic solvents (O_T), whereas it is possible to be degraded and extracted by the alkaline treatment applied during the $1O_2$ and $2O_2$ stages. Therefore, it was justified the inclusion of the lignin precipitation stage after the $1O_1$ stage. On the

contrary, the fraction of L3 recovered after the $2O_2$ stage was inefficient, based on the low extraction yields (0.5-2.5% for all the materials). Thus, this fraction could be considered almost negligible.

Hemicelluloses recovery resulted in low yields regardless of the feedstock. This is caused because for hemicelluloses (H1, H2, and H3), only solid fractions were considered, not the small fractions (sugars and acids) that were not capable of being precipitated by the method described before. In any case, the extraction stages (A_P y O_T) were intentionally designed using mild conditions to allow the extraction of the hemicelluloses without degrading them into their monomeric compounds. H1 and H2 were the precipitated fractions from A_P and O_T, whereas the H3 was comprised in the solid fraction in the final recovered pulp after the bleaching sequence. This is why H3 obtained a higher recovery yield since only the bigger molecular compounds of the extracted hemicelluloses could be isolated by this precipitation method. While this technique could not recover the monomeric sugars and small oligomers, which were neglected due to the low concentration, it was quantified in the liquid streams and their difficulty to be valorized in value-added applications. This is due to their lack of biocompatibility based on the pH of the extracted liquid streams, despite the approach followed in other works (Gullón et al., 2020). Consequently, the most remarkable yield was reached by To, because the remaining hemicelluloses after the thermal treatment are more condensed and more accessible to be isolated by their precipitation, despite their lower composition in the feedstock.

Regarding process efficiencies (the total amount of solids recovered after fractionation), they were similar during the first two processes: the process efficiency of Organosolv 84.18% and the first alkaline extraction 85.19 % (tables S2 and S4 respectively of supporting information). During the second alkaline extraction, the efficiency was almost 100%, while the recovered lignin was, in every case, less than 1 g_l g_m^{-1}; the recovered solid fraction was practically not changed. This can be related to the process reaching its inherent feasibility to extract lignin, a phenomenon observed in previous work from De Hoyos-Martínez and collaborators (de Hoyos-Martínez et al., 2018), and less pronouncedly in the work of Fernández-Rodríguez and collaborators (Fernández-Rodríguez et al., 2017b), in which sequential treatments of similar nature resulted in considerably lower yields. Process efficiencies of hydrogen peroxide stages (P) correspond to the recovered bleached pulp, as no other product could be recovered; in the case of the first stage (P_Q), the mean process efficiency was 75.51%, being 83% for pinewood and 72% for thermowood. It can be appreciated that the total lignin recovered corresponded to a total of 98.63 % for Po and 61.00% for To without weathering, while the recovery of lignin after weathering was 51.19% for Pw and 58.94% for Tw. This implies that the lignin recalcitrance for extraction with the Organosolv and $1O_2$ bleaching stage does not change after weathering for T samples, while for P, it has an important decrease in the effectiveness during the $1O_2$ stage.

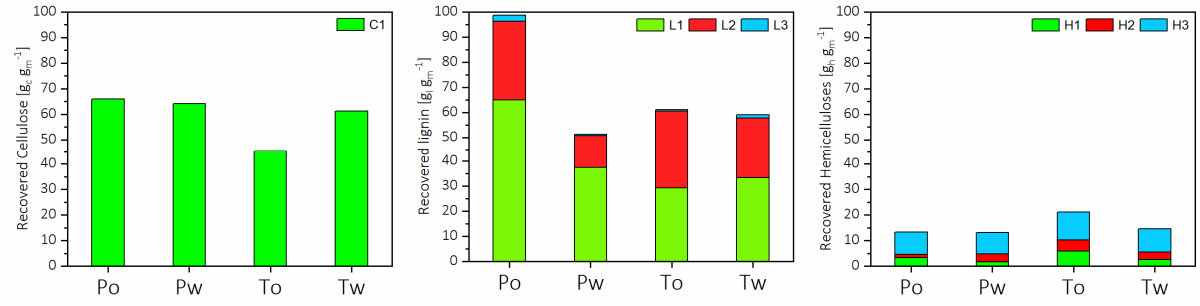

Figure 3. Yields of each recovered solid fraction concerning the initial macrocomponent amount reported in Figure 2. C1 is the cellulose content of the bleached pulp. L1 is the organosolv lignin, L2 is the alkaline lignin from bleaching sequence O1, L3 is the lignin from bleaching sequence O2. H1 is the hemicelluloses from acid pretreatment, H2 are the hemicelluloses from organosolv, and H3 are hemicelluloses remaining in the bleached pulp.

3.3. Physico-chemical characterization of the obtained products

3.3.1. Cellulose fraction

Infrared spectrometry analysis was performed on the cellulose fractions recovered to evaluate their structure (Figure 4). Infrared spectra of bleached pulp (C1) show a broad band at 3600–3000 cm^{-1}, attributed to free vibrating hydroxyl groups characteristic of cellulose. Bands corresponding to *v*(C-H) and *v*(CH_2) locate between 3000-2800 cm^{-1} displayed a weak intensity before thermal treatment of wood; in the case of To and Tw, they are almost imperceptible. Regarding the fingerprint region, it can be identified a band at 1430 cm^{-1} related to Methoxyl–O–CH_3 bonds and a band at 1370 cm^{-1} corresponding to C-H bond in –O(C=O)CH_2 group. Bands at 1317 and 1200 cm^{-1} are attributed to -OH groups in-plane bending, while the band at 1160 cm^{-1} corresponds to the C-O-C anti-symmetric bridge stretching in cellulose. Below 1200 cm^{-1}, there can be identified two bands at 1100 and 1055 cm^{-1} corresponding to C-OH and C-O stretching, and finally, a band at 900 cm^{-1} that corresponds to the β-glucosidic linkages between sugar units (Kruer-Zerhusen et al., 2018). In this fingerprint region, there is no particular difference between the analyzed celluloses, which implies that the chemical structure of cellulose is not significantly affected by either the thermal treatment or the effects of weathering.

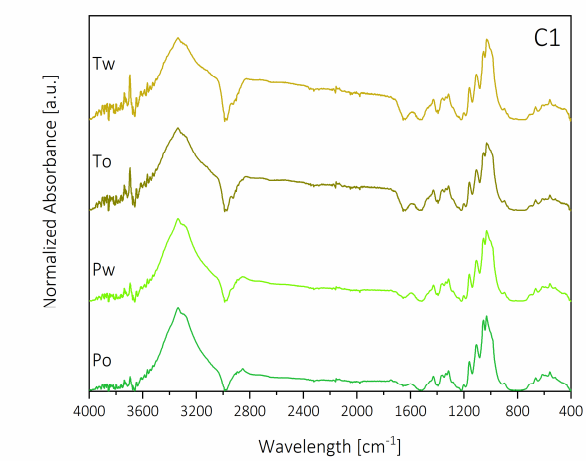

Figure 4. Infrared absorbance spectrograms of the obtained celluloses.

Figure 5 presents the ^{13}C CP-MAS NMR analysis of the obtained bleached pulps, composed mainly of cellulose. Insets present a magnification of the C4 region, which is considered a referent to identify the more ordered structures of cellulose I. NMR analysis shows that the structure of pulps was practically invariable despite weathering. This consistency was a positive outcome if weathered thermally treated wood would be considered as raw material for the pulp and paper industry during a cascading use of such material. The main difference observed was between Po and Pw, with an increase of the amorphous region of the C4 chemical shift, while for To and Tw, the change in proportions was inverse, with Tw having a sharper shift at the ordered region (92-86 ppm). This change can be related to the transformation of low molecular carbohydrates during treatment, which reacted with lignin and leached during weathering. This resulted in a pulp enriched in more crystalline and ordered cellulose, which is a phenomenon already reported to happen in thermally treated wood regardless its origin (softwood or hardwood), previous authors have reported maximal crystallinity being reached around 210 °C, similar to the conditions used in this work (Durmaz et al., n.d.; Yildiz and Gümüşkaya, 2007).

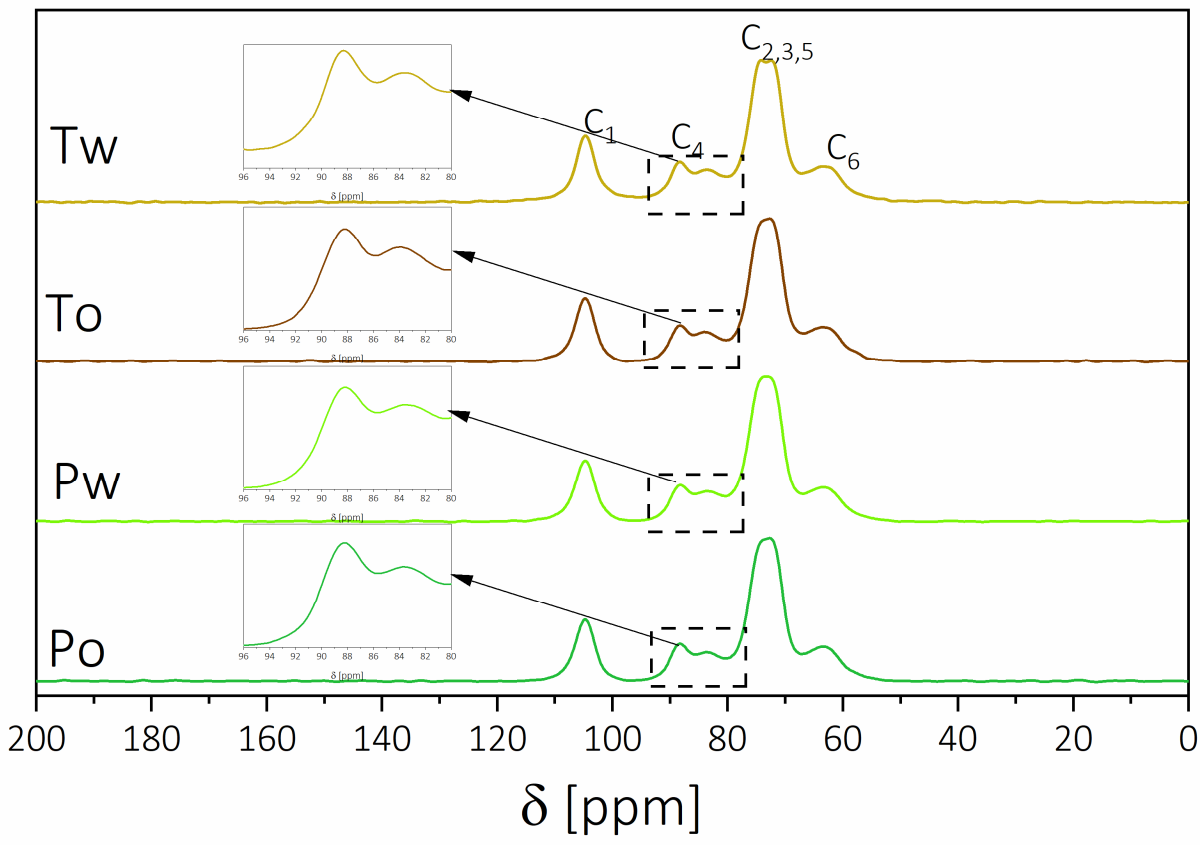

Figure 5. NMR spectra of the obtained celluloses

The x-ray diffraction patterns of the bleached pulps are presented in Figure 6. Three main components can be observed, cellulose Iβ, which was the major component, as it is typical for native celluloses, cellulose Iα in a minor proportion, and traces from $Mg(OH)_2$, which were residuals from the first alkaline-oxygen bleaching stage. As calculated from the XRD patterns with the peak fitting method and subtracting the contribution made by $Mg(OH)_2$, crystallinities were in general high, with Po having 70.4%, Pw 68.25%, To73.69, and Tw 71.48%. This means that crystallinity was slightly increased during thermal treatment, mainly due to interaction between amorphous cellulose with lignins to form lignin-carbohydrates complexes (LCC), but it was also reduced after weathering because of cellulose degradation. It can be concluded that there was a direct relationship between the crystallinity of the cellulose and its affinity to keep $Mg(OH)_2$ attached to the pulp when comparing results

from Figures 5 and 6. Po and Tw were the ones having more intense signals corresponding to the $Mg(OH)_2$ (Maskal and Thompson, 1971; Ni and He, 2004).

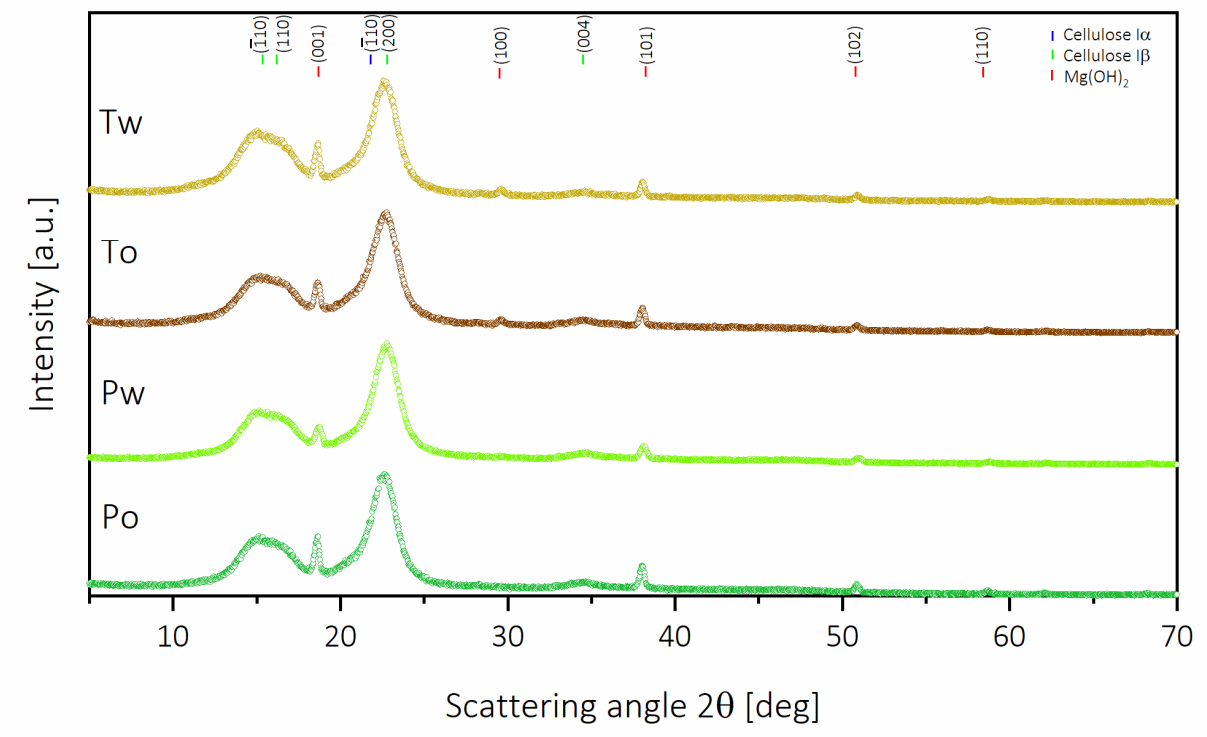

Figure 6. X-ray diffraction patterns of the different celluloses.

3.3.2. Hemicellulose fraction

Pure hemicelluloses streams were recovered from two different stages of the global process; leaching (H1) and organosolv (H2), as H3 was contained within the final pulp stream. Their monomeric composition characterized these precipitates both in sugars and in acids, whose quantified amounts are presented in Table 1. The most common sugar was mannose-related oligosaccharides, as expected from softwood (Santos et al., 2018). The presence of mannose in H1 was affected by two parameters. First, the thermal treatment, showing a decrease of ≈37% in To compared to Po, and the second was the weathering, having Pw a decrease of ≈23% compared to Po. When both parameters were present (Tw), the decrease in mannose concentration was ≈51%. This means that, while the cellulose was preserved almost identical through the treatment and weathering, the oligosaccharides present in the pinewood were more severely affected by these two parameters, with xylose concentrations and arabinose oligosaccharides suffering similar tendencies in the case of H1. On the other hand, H2 samples were more similar; however, the overall purity was strongly diminished; this is due to the severity of the treatment, but also because of the difficulty to recover dissolved polysaccharides from organosolv liquors, given the fact that hemicelluloses precipitate in organic solvents (Peng et al., 2012).

Table 1. The concentration of monomeric sugars and acids in the recovered products (expressed in mg L^{-1}).

	H1				H2			
	Po	Pw	To	Tw	Po	Pw	To	Tw
Xylose	5.21	2.32	1.11	2.19	0.13	0.45	1.34	2.36
Arabinose	3.99	2.71	1.15	2.22	1.81	0.58	2.20	2.83
Acetic acid	3.03	2.47	9.71	3.52	6.41	2.00	2.84	10.47
Formic acid	-	-	3.34	-	-	1.99	-	-
Mannose	45.31	34.75	28.38	22.07	14.84	12.95	13.63	12.72

The infrared spectra of hemicelluloses obtained from the acid leaching (H1) presented a broad band at 3600-3000 cm^{-1} corresponding to hydroxyl groups stretching of the mannose and xylose units in hemicellulose

molecules. A band at 2000-2700 cm^{-1} corresponded to -CH bond deformation of $-CH_2$ and $-CH_3$, these bands were absent in To and Tw, meaning that most of the hemicelluloses were depolymerized during the hydrothermal treatment (Boonstra and Tjeerdsma, 2006). The spectra of H1 from To and Tw were more similar to xylose, showing weaker bands attributed to C-H vibrations of mannose (1500-1200 cm^{-1}) than Po and Pw, and weak peaks associated with xylose (1200-900 cm^{-1}), thus showing xylose degradation (Wang et al., 2013). Hemicelluloses obtained from the Organosolv treatment (H2) presented fewer differences between each other. Thus, increasing the severity of the treatment, the obtained samples were more homogeneous regardless of the used feedstock in the process. In H_2, it can be highlighted the identifiable bands corresponding to hydroxyl groups (3600-3200 cm^{-1}), the band at 1650 cm^{-1} corresponds to CO stretching of carboxylate in either salt or ester form (Z. Chen et al., 2015). Finally, characteristic C–O–C stretching of the pyranoid ring of xylan was observed at 1060 cm^{-1}, and the band corresponding to β-glucosidic linkages between xylose units is present at 890 cm^{-1} (Sun et al., 2013). Results from infrared spectra were concurrent with the concentration analysis, showing a reduction in mannose concentration for H1 in To and Tw compared with Po and Pw; while for H2, the spectra presented lower variations.

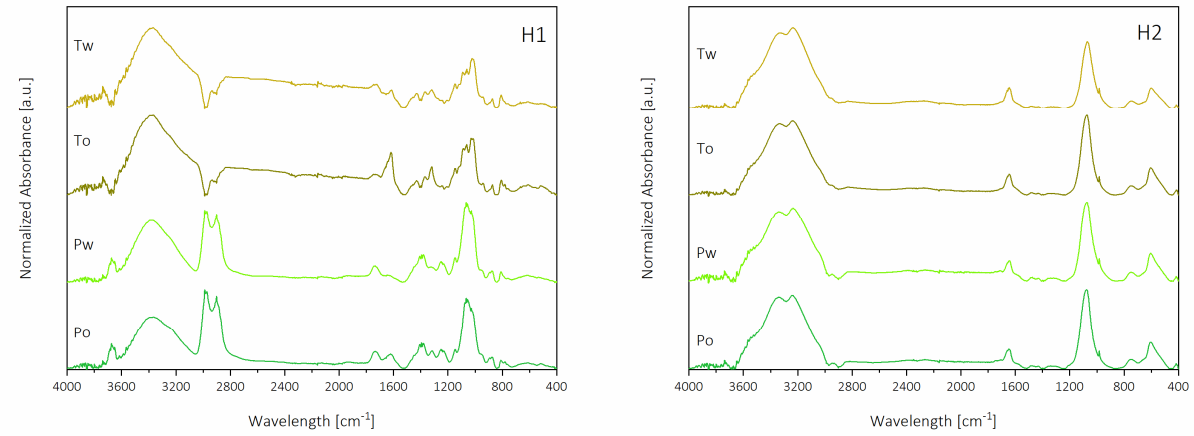

Figure 7. Infrared absorbance spectrograms of the obtained hemicelluloses from acid pretreatment (H1) and organosolv (H2).

3.3.2. Lignin fraction

Table 2 presents values corresponding to acid-insoluble lignin (AIL), acid-soluble lignin (ASL), residual carbohydrate contents, ashes, molecular weight (Mw), and polydispersity index (Mw Mn^{-1}) of the obtained lignin samples. The aggregate of ASL and AIL is related to the purity of the obtained lignin, in which it can be observed a high purity of the organosolv lignins (L1) with no significant differences between the samples extracted from the different feedstock (93-95% for all of them). This means that despite the differences between yields, the properties of lignins obtained by the O_T stage shared the same composition. Besides, the higher purity of the isolated lignin, compared to other results presented in the literature (Hosseinaei et al., 2016; Toledano et al., 2013), could be based on introducing the pretreatment stage, where the carbohydrate compounds that could pollute the lignin samples were significantly reduced by the A_p stage; in line with other similar works previously carried out by this research group (Fernández-Rodríguez et al., 2017a). This was also countersigned by the low presence of sugars in the collected samples, with values between 1.70 and 1.85% except for Tw lignin, in which the carbohydrate content of the lignin samples was above 2.5%. This increase can be related to the recalcitrance caused by the LCC formed during the thermal treatment, which were not leached during weathering neither hydrolyzed during the A_P treatment. This tendency was also observed in alkali lignins from the first bleaching step (L2), in which both weathered samples (Pw and Tw) presented higher carbohydrate content than their original counterparts, following the same trend already reported in previous work (Fernández-Rodríguez et al., 2017b). In any case, the purity of the L2 samples was above 90% (except in the case of Po), demonstrating once again that the inclusion of a lignin isolation step could be implemented even during the first bleaching stage since the purity of the lignin was not compromised. Nevertheless, the lignin precipitation from the $2O_2$ stage was

not justified due to the low amount obtained, which was not big enough to obtain the necessary material even to conduct its full characterization.

Figure S2 shows a graphical display to explain better the occurring tendencies regarding molecular weight and polydispersity index. In the untreated pinewood, the molecular weight of lignins after weathering was higher in all cases (L1, L2, and L3), presenting an almost linear trend and, therefore, a correlation between the Mw of each lignin type. The Mw of organosolv lignin (L1) in all samples was decreasing after thermal treatment, as it is represented in Figure S3. On the contrary, the Mw of alkali lignin (L2) increased after the thermal treatment of the samples.

Table 2. Composition of the lignin samples collected along the different stages of the experimental procedure.

		AIL [%]	ASL [%]	Carbohydrates [%]	Ashes [%]	Mw [g mol^{-1}]	Mw Mn^{-1}
Po	L1	93.4	0.88	1.84	1.13	5534	4.43
	L2	83.3	1.46	3.01	1.15	2772	2.94
	L3	-	-	-	-	21,936	12.4
Pw	L1	93.9	0.53	1.83	0.29	7401	5.32
	L2	93.1	1.20	4.44	0.65	10,049	8.68
	L3	-	-	-	-	28,573	9.27
To	L1	93.4	0.74	1.73	0.51	1453	2.36
	L2	92.8	1.08	5.27	1.06	3477	4.16
	L3	-	-	-	-	23,380	12.8
Tw	L1	94.6	0.95	2.58	0.25	4307	3.71
	L2	89.9	1.29	6.11	0.49	3465	3.88
	L3	-	-	-	-	19,233	10.3

All the lignin samples (L1, L2, and L3) were subjected to infrared analysis and carbohydrate products. Besides having different yields depending on the stage from which they were recovered, there were noticeable differences between the three of them according to their functional groups, with more differences found depending on the source. Absorption band associated with -OH stretching vibrations of aromatic and aliphatic groups between 3700 and 2900 cm^{-1} presented a distinct difference for L1. On the other hand, for L2, the intensity of that absorbance band was lower in the case of To and Tw compared to Po and Pw, and in the case of L3, the presence of the OH band was almost imperceptible. The bands between 2900 and 2750 cm^{-1}, which correspond to CH stretching in $-CH_2$ and $-CH_3$, were more intense in the case of bleaching-stage lignins (L2 and L3) than in Organosolv lignin (L1). Moreover, in L1, the C-H band was more acute for To and Tw, which correlated with the absence of such bands in H1. This phenomenon can be related to the formation of LCC during hydrothermal treatment. The band at 1710 cm^{-1}, identified with non-conjugated carboxylic acids, was present in all lignins, with a tendency to decrease after each treatment (L1>L2>L3). Another particularity was the increase of the intensity of this band for To and Tw in the case of L1, which can be related to the degradation of small carbohydrate sugars into carboxylic acids. The band between 1700 and 1400 cm^{-1} was related to the aromatic skeletal vibrations of lignin. In this region, the same decreasing tendency can be observed, which implies a lower quality of lignin found during the cascading recovery. In this region can be highlighted the band at 1595 and 1510 cm^{-1}, which corresponds to C=C linkages of the skeletal aromatic ring, the band at 1460 cm^{-1} corresponding to C-H deformation, and the band at 1420 cm^{-1} corresponding to C-H aromatic ring vibrations. In the region between 1500 and 1000 cm^{-1}, the prominent guaiacyl lignin bands can be identified, namely 1270, 1120, and 1030 cm^{-1}, which are related to v (C-O stretching) of the guaiacyl ring, v(C-H stretching) of the guaiacyl unit, and v(C-O and C-H) in-plane deformation of G-type lignin respectively (Derkacheva and Sukhov, 2008; Fernández-Rodríguez et al., 2017b; Ibarra et al., 2007; Lu et al., 2017; Xu et al., 2013). These bands presented a gradual decrease after each treatment, with the first alkali extracted lignin (L2) from hydrothermally treated wood (To and Tw) having the weakest absorbance intensity in this region.

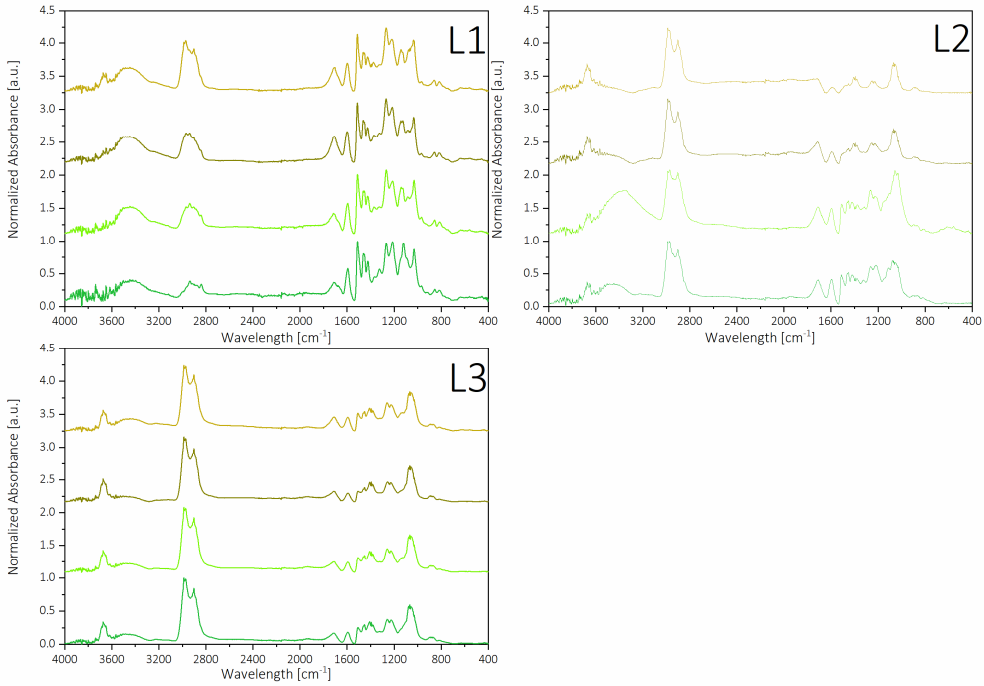

Figure 8. Infrared absorbance spectrograms of the obtained lignins.

The thermal properties of the different lignin samples were subjected to a thermogravimetric (TG) analysis. Figure 9 presents the thermograms of L1 and L2 lignins under an inert atmosphere; insets show the derivative thermogram. Other parameters, such as the temperatures of 5% mass loss, 50% mass loss, and residues after 800 °C, are represented in Figure S4. Regarding the amount of the remaining residue, the main difference was appreciable between the final residue for L2 compared to L1, as L2 residues are between 42.39% (Po) and 51.09% (To), while L1 residues are between 33.36 (Po) and 39.74 (Tw). This situation was related to the origin of the lignin since more condensed structures were expected from the $1O_2$ stage against L1 from O_T. Besides, it can be highlighted that there was a clear tendency to increase the residue at 800 °C for thermally treated wood, regardless the stage the lignin samples were isolated (L1 or L2). This can be based on the more stable lignin is conformed during the thermal treatment, as it was commented before. The TG analysis under inert atmosphere gives information regarding the potential char production for each lignin; therefore, a higher residue was related to a higher char content. The differences in decay temperatures and the thermal stability of lignins are related to their structure, molecular weight, origin, and the extraction and precipitation methods followed to obtain the lignins (Gordobil et al., 2016). In this sense, L1 presented higher thermal resistance, presenting the maximum degradation temperature at higher temperatures than those of L2. It can also be seen that To and Tw had higher thermal resistance than Po and Pw. Moreover, Pw and Tw had higher maximum degradation temperatures than Po and To, respectively. On the other hand, L2 lignins presented lower differences between Po and To, being Pw, the one with the highest thermal maximum degradation temperature (389 °C), lower than all of the L1 lignins. From the TG analysis, it can be concluded that L2 lignins were more prone to produce char than L1 samples. This can be due to the O_T stage being more effective in extracting less altered lignin structures. Simultaneously, the oxidizing effect of oxygen, hydrogen peroxide, and the alkaline media influence the denaturalization of these compounds, resulting in lignins with more condensed structures.

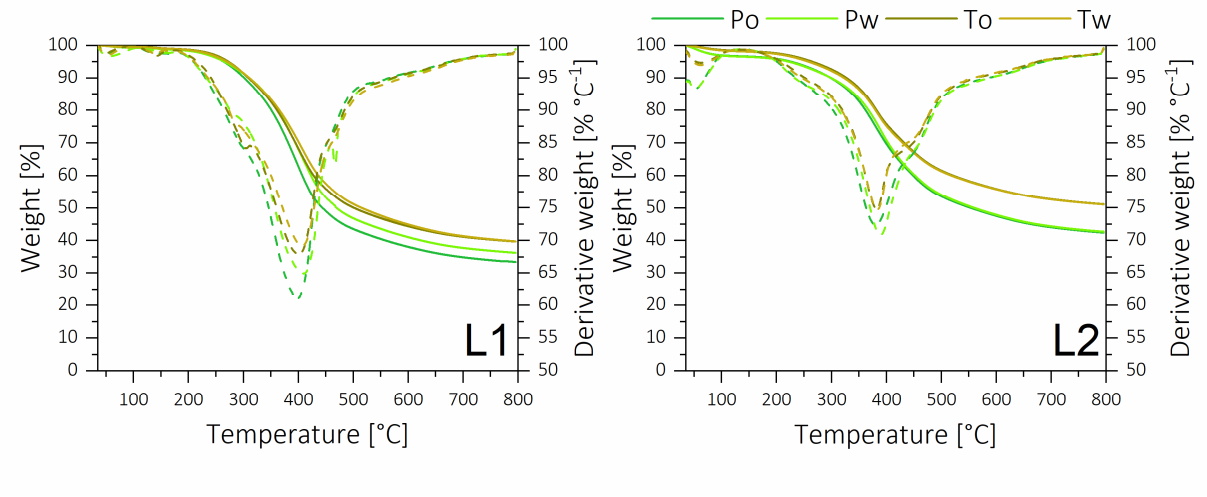

Figure 9. Thermograms and derivative weight loss as a function of the temperature of L1 and L2 of the different samples.

To conclude the lignin characterization, the structural composition of the lignin samples was analyzed by the Py-GC/MS technique. The analysis is carried out based on the work developed by Chen and collaborators (L. Chen et al., 2015). The identified phenolic derivatives were classified into five categories, namely benzene (B), phenol (P), catechol (C), guaiacol (G), and syringol (S) derived units. As it is not clear that catechol could be originated from G or S structures, the results were also expressed as the S/G ratio to facilitate the interpretation of the results. Guaiacol was the main compound identified by this technique, a typical fact in lignin samples obtained from softwood species. Thus, the S/G ratio was always close to zero. The highest values were obtained by Po lignin samples regardless of the stage they were isolated from (L1 and L2). This indicates that both the thermal treatment and the weathering attack to a more prominent degree the S units, since the natural weathering of wood (especially UV radiation) and thermal treatment could promote demethoxylation reactions that resulted in the transformation of S derived units into C and G derived moieties. This tendency has already been reported (Ma et al., 2016). The G units lead to creating more condensed structures due to their availability of the C5 in the aromatic ring. Lignin samples from To feedstock show the second highest values; thus, weathering causes this degradation mechanism to a higher degree than the thermal treatment. Among samples from different stages, the differences were not significant, although there was a trend to reduce the S/G in L2 samples in comparison with L1, a fact that can be explained for the mechanisms described before since, during the 1O2 stage, more demethoxylation reactions of the S units could appear. Moreover, they followed a similar decreasing tendency in both organosolv and alkaline lignins after the weathering treatment.

Table 3. The abundance of the different phenolic-derived units in the lignins respects the total phenolic moieties detected.

		Benzene	Phenol	Catechol	Guaiacol	Syringol	S/G ratio
L1	Po	0.26	3.47	2.67	81.4	12.2	0.15
	Pw	0.10	5.49	8.71	83.9	1.82	0.02
	To	0.00	4.14	9.34	76.1	10.4	0.14
	Tw	0.00	7.01	10.1	82.9	0.00	0.00
L2	Po	0.21	3.40	5.97	80.2	10.3	0.13
	Pw	0.27	4.41	5.8	87.2	2.37	0.03
	To	0.20	4.02	8.32	83.8	3.69	0.04
	Tw	0.00	3.51	6.60	89.0	0.93	0.01

Conclusions

The present work proposed a cascade valorization of thermally treated wood after service-life by fractioning its macromolecular components through green processes. To assess the quality of the obtained materials, they were compared with untreated wood and unweathered counterparts. Results showed that the macromolecular constituent that presented the most stability regardless of the conditions was cellulose, having little structural properties changes regardless of the feedstock used as raw material, which demonstrated the robustness of the designed process as the main product in yield was very homogeneous, a fact that would enable the scalability of this global process. The extracted hemicelluloses consisted of high purity mannose oligomers; however, due to the difficulties of precipitating hemicelluloses in its polymer nature, the use of the organosolv process and the acid leaching were not enough to justify a valorization of hemicelluloses, as their low extraction yields demonstrated it. Lignins were the macromolecules presenting more variations, with significant differences depending on the extraction phase (organosolv pulping or oxygen-alkali bleaching) and the material source. With thermally treated wood having more LCC (oxygen-alkali lignin) but also the best yield of AIL (organosolv lignin), however, in general, the purity and the thermal stability of all the lignins resulted in high values for either lignin, stating that the selected processes are robust and appropriate for the fractioning of pinewood after being thermally treated and weathered.

Supporting Information.

Please consult the supplementary information for additional data.

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