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Fractionation of non-timber wood from Atlantic mixed forest into high-value lignocellulosic materials

Leyre Sillero, Sebastián Barriga, Nagore Izaguirre, Jalel Labidi, Eduardo Robles*

Biorefinery Processes Group, Chemical and Environmental Engineering Department, Faculty of Engineering Gipuzkoa, University of the Basque Country UPV/EHU, Plaza Europa 1, 20018 Donostia, Spain

The forestry industry in the Basque Country has experienced an abandonment of small-sized forests in which native and introduced species tend to regrow if unattended, thus requiring an intervention under which proper forest management is implemented. The present work evaluates the potential fractionation of lignin and cellulose of six tree species coming from such mixed forests as a value-added utilization of wood discarded for logging within the frame of sustainable forest management. The used species were Northern red oak, common oak, common ash, Iberian white birch, sweet chestnut, and black locust. The different wood samples were treated with an Organosolv treatment and elemental chlorine-free bleaching to fractionate them to their main components, recovering the cellulose and the lignin. Cellulose was defibrillated via high-pressure homogenization to obtain cellulose nanofibers. The obtained lignin and cellulose nanofibers were analyzed. The obtained results support the idea that this process offers the opportunity to treat the different raw materials in the same process, with the corresponding possible economic benefits.

Keywords: Atlantic mixed forests; Organosolv treatment; cellulose nanofibers; lignin

1. Introduction

The forest area of the EU-27 was 177.76 million hectares in 2010, of which 27.747 million correspond to Spain, placing it in the second country of the EU-27, behind Sweden (with 31.247 million hectares). Within Spain, the percentage of forest areas in the Basque Country situates the Autonomous Community at the fifth community behind the Balearic Islands, La Rioja, Cantabria, and Madrid. Moreover, data from the Yearbook of Forest Statistics for 2011 reveal that the Basque Country is the fifth community with the most significant presence of forest area in relation to the whole of its geographical area [1, 2]. In the Basque Country, forests cover more than 492,233 hectares [3], which is 68% of the territory. Of this, the wooded area covered 396,962 hectares as of 2010, representing approximately 54% of the surface of the Basque Country, which is one of the highest ratios in the European Union [1]. This percent has

further increased up to 54.94 % as of 2016 [4]. The forestry sector in the Basque Country has developed throughout the late 19th century and the whole 20th century through plantations. The species most used in plantations have been Pinaceae, which were grown mainly during the 1950s up to the 1970s [5]. However, this boom stopped by the mid-1970s and was stabilized for almost twenty years, after which it started to decay by the mid-1990s. The abandonment of old pine plantations or pasture areas has provoked the growth of the Atlantic mixed forest, mostly from the trees that have grown under cover of forest plantations. This kind of forest is composed by masses that are very widespread on the Atlantic side of the Basque Country and are generally small (less than 2 ha) with the property corresponding mainly to private hands. The trees in this formation are in general of small size, mainly of classes with lower diameter. In recent years, the density of these plots has continued to increase due to the absence of forestry interventions. Given the predominantly private ownership of these surfaces and the current state of abandonment of a large part of them, it is considered a priority to establish special mechanisms to encourage forest management.

The denomination of the Atlantic mixed forest contains a large number of typologies and problems, which makes it challenging to adopt standard management guidelines for all these areas. However, it is understood typically as a heterogeneous mixture of diverse hardwood species, which emerges after a cleaning cut or agricultural abandonment from stumps and seeds, growing below 600 m above sea level. The heterogeneity of these forests is such that none of the species extant hardly represents higher than 10% of the total forest. Currently, mixed forest surfaces have been estimated to be 47,929 ha (2016), with an increase during the period between 1996 and 2016 that ranges between 30 and almost 50% depending on the region [6].

In the Basque Country, 55.34% of the forested area is composed, in order of importance, by radiata pine plantations, beech forests, and the Atlantic mixed forests. These three primary forests, along with Valencian oak (*Quercus faginea*) forests and holly oak (*Quercus ilex*) forests, make up to 70% of the surface of the Basque forests [1]. Regarding the forest species present in the Atlantic mixed forests, some of the most common are: common oak (*Quercus robur*), sweet chestnut (*Castanea sativa*), black alder (*Alnus glutinosa*), Iberian white birch (*Betula pubescens*, var celtiberica), common hazel (*Corylus avellana*), black locust (*Robinia pseudoacacia*) and common ash (*Fraxinus excelsior*). Some of these woods have a high potential value as log timber for different applications; however, proper management of the forest would require cutting and pruning, which is an intense and demanding work that gives no economic retribution to landowners until they cut down the final trunks, thus representing an underestimated asset or a by-product. In case of the Basque Country, current silvicultural systems consist, depending on the size of the forest, in clear-cuts (<0.5 ha), shelterwood cutting and intensive pruning (0.5–6 ha), shelterwood cutting and extensive pruning (6–20 ha) and shelterwood cutting and extensive pruning by stands (>20 ha).

The valorization of biomass by-products has become a subject of particular interest due to its great potential as a source for chemical products and high value-added biomaterials. Additionally, biorefineries are a competitive alternative to traditional oil refineries, especially in those countries that lack fossil resources [7–9]. For this reason, the biorefinery is considered as the economic engine that drives society to achieve sustainable development through the conversion of lignocellulosic biomass into energy, fuels, and chemical products [10]. Organosolv is one of the most desirable processes to achieve an integrated biorefinery. These methods are based on the solubilization of lignin by using different organic solvents and water

as cooking liquor, extracting highly homogeneous lignin, which enables its further valorization into value-added products [11, 12]. The use of Organosolv processes not only is better in terms of the environment, but it also allows the possibility to recover solvents through evaporation[13].

In the case of biomaterials, two main components can be fractionated from lignocellulosic biomass. Moreover, there has been increasing attention on the potential use of cellulose to obtain nanocellulose, a renewable, cheap, and non-toxic bio-based material with widespread applications [14, 15]. Nanocellulose possesses extraordinary physical, thermal, and mechanical properties, such as high specific surface area and high modulus of elasticity [16]. Lignin is the second main product that is fractioned from biomass; however, it has been used traditionally for energy recovery (pyrolysis). Nonetheless, in recent years it has attracted the interest of the industry and the scientific community for its properties, its high availability, and its low price [17].

The present work seeks to provide an alternative to the management of abandoned Atlantic mixed forests (multi-species forest), currently representing a low interest for traditional pulp and paper industries (high content of diverse hardwoods) which is one of the mains second transformation processing of wood biomass in the Basque Country. For this, wood from different tree species from the Atlantic mixed forest was selected for characterization and fractionation into lignin and cellulose nanofibers, which were characterized to explore their potential valorization through a biorefinery approach, as well as the possible combined fractionation of all that different raw materials.

2. Materials and Methods

2.1 Materials

2.1.1 Raw material

Basoekin Ltd kindly provided different wood samples collected from local forests. These corresponded to Northern red oak (*Quercus rubra*), common oak (*Quercus robur*), common ash (*Fraxinus excelsior*), Iberian white birch (*Betula pubescens, var celtiberica*), sweet chestnut (*Castanea sativa*), and black locust (*Robinia pseudoacacia*). All samples corresponded to young stands (11-18 years) except for red oak (~60 years). Samples were firstly debarked and milled into chips (sieved to 0.5 × 0.5 mm) using a Retsch Cutting Mill SM 100. The chemical composition of the raw materials was carried out according to standard methods of the Technical Association of the Pulp and Paper Industry and the National Renewable Energy Laboratory (moisture, ashes, extractives, carbohydrate content, and lignin) [18–21], as well as traditional methods (α-cellulose and hemicelluloses as the difference between holocellulose and α-cellulose) [22, 23].

2.1.2 Chemicals

Gallic acid, Folin-Ciocalteu phenol reagent, sodium carbonate, and ethanol were purchased to Sharlau (Spain). Panreac AppliChem supplied sulfuric acid, sodium hydroxide, magnesium sulfate sulfuric acid acetic acid (glacial), hydrogen peroxide, dimethyl sulfoxide, and sodium chlorite. Toluene and dimethylformamide were purchased from Fischer Scientific and N, N-bis (carboxymethyl) glutamic acid was purchased from Alfa.

2.2 Fractionation methods

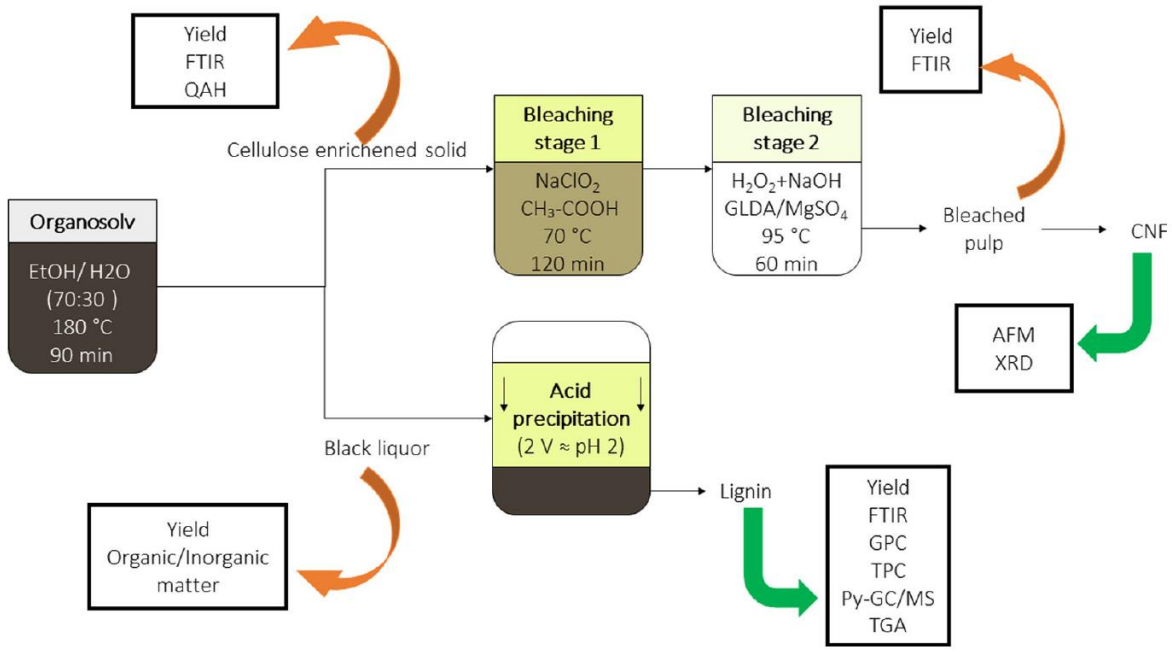
2.2.1 Organosolv treatment

Wood samples were subjected to an organic solvent treatment, carried out using an ethanol-water mixture (70:30 v/v); the process, selected according to the chemical composition of the raw materials, occurred at 200 °C with an internal pressure stabilized at 30-32 bar. The reaction was carried out for 90 minutes with constant stirring (200 rpm) and continuous cooling to avoid overheating [24]. Black liquor was separated from the solid fraction by filtering the cooked mixture with a Buchner funnel system using an MN 640w filter paper. Precipitation of the liquors was done by adding two volumes of acidified water (pH ~ 2) at 5 °C, allowing the precipitation process to stand for an average of 4 hours inside a cold bath. Precipitated lignin was filtered with a Buchner funnel system using a 0.22 µm nylon membrane, collecting a sample of the first filtrate for subsequent analysis. Then, the lignin was washed once with acidified water to remove remaining impurities and then with distilled water until neutral pH was reached. The lignins obtained after being filtered were dried and stored for further characterization.

2.2.2 Pulp bleaching

The cellulose enrichened solid was bleached with a two-stage bleaching sequence. The first stage consisted of bleaching with sodium chlorite ($NaClO_2$), and the second used hydrogen peroxide (H_2O_2). In the bleaching with sodium chlorite, for every 100 grams of pretreated fibers, 104 mL of sodium chlorite (23% by volume), 20 mL of glacial acetic acid, and 876 mL of water per gram of cellulose were placed in a 1 L glass media bottle. The reaction was done at 70 °C in a water bath in which the closed bottles were introduced, and the treatment was carried out for 2 hours, mixing the solution every 30 min. The fibers were then filtered and washed until neutral pH. For the bleaching with hydrogen peroxide of fibers, 727 mL of

water, 262 mL of hydrogen peroxide (35% by volume), 1.67 g of N, N-bis (carboxymethyl) glutamic acid (GLDA, chelating agent), 4 grams of sodium hydroxide, and 5 grams of magnesium sulfate ($MgSO_4$) were added per each 100 grams. The reaction was carried out at 95 °C for 60 minutes in a water bath, after which the mixture was filtered and washed to neutral pH using an ash-free filter paper and dried in an oven at 50 °C. A synthesis of the fractionation methods is shown in Scheme 1



Scheme 1. Process flowchart of the chemical pulping and bleaching.

2.1.3 Elaboration of cellulose nanofibers

Cellulose nanofibers were made by disintegrating the cellulose suspension with a high shear homogenizer Heidolph Silent Crusher M for 10 minutes at 20,000 rpm and then passing the slurry through a Niro Soavi high-pressure homogenizer (HPH) 10 times at 500-600 bar.

2.3 Characterization of the obtained products

The obtained products were characterized to assess their yield and quality. Both cellulose and lignin were analyzed by FTIR spectroscopy; moreover, celluloses were analyzed in terms of

their Segal crystallinity index, and nanocellulose was analyzed by atomic force microscopy. Lignins were characterized by their total phenolic content, their S/G ratio, their mass average molar mass and polydispersity, and their thermal stability. These characterizations allow determining the differences between the obtained products.

2.3.1 Yields and purity of the obtained components

The assessment of the recovered solid matter for each product was carried out by gravimetric analysis. The cellulose content of the bleached pulps was evaluated according to the standard method [25]. The acid-insoluble lignin (AIL), the acid-soluble lignin (ASL), and the carbohydrate content were measured following the method used by Davila et al. [26] and NREL laboratory procedure [21]. Samples were characterized using UV equipment (Jasco V-630) with a of 10 mm light path using UV quartz cuvettes (ASL), and a high-performance liquid chromatograph Jasco LC-Net II/ADC equipped with an Aminex HPX-87H with 300 x 8.7 mm (Bio-Rad Laboratories, USA) column and refractive index detector (carbohydrate content).

2.3.2 Infrared spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) was performed to analyze the main chemical bonds present in lignins. The spectra were recorded on a PerkinElmer Spectrum Two FTIR spectrometer equipped with a universal attenuated total reflectance accessory with an internal reflection diamond lens. The defined range has been from 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1}. For each sample, 20 sweeps have been recorded.

2.3.3 X-ray diffraction

The crystallinity of cellulose samples was analyzed by X-ray diffraction. The X-ray patterns were collected with a Panalytical Phillips X'Pert PRO multipurpose diffractometer, with

mounted samples in a zero-background silicon wafer attached to a generic sample carrier, using monochromatic CuKα radiation (λ = 1.5418 Å) in a 2θ range of 5 to 70 with a step size of 0.026 and 80s per step at room temperature. The following equation was used to calculate the Segal CI (%):

$CI = 100 \times (I_{200} - I_a)/ I_{200}$

Where I_{200} is the total intensity of the (200) peak for cellulose I, and I_a is the amorphous intensity at ~18° 2θ for cellulose. The inclusion of the Segal index, whether it can be controversial, is still the main qualitative referent in literature [27].

2.3.4 Morphology of the obtained nanofibers

Atomic force microscopy images were obtained by operating in pulse mode with a NanoScope IIIa, Multimode TM-AFM from a Veeco scanning probe microscope from Digital Instruments equipped with an integrated silicon tip cantilever with a 300 kHz resonance frequency.

2.3.5 Gas chromatography-mass spectroscopy with pyrolysis

The lignin samples were characterized by gas chromatography-mass spectroscopy with pyrolysis (Py-GC/MS). The Py-GC/MS was carried out following the method described by this group [28] using a pyrolyzer (Pyroprobe model 5150, CDS Analytical Inc., Oxford, PA). Between 400 and 800 μg was pyrolyzed inside a quartz crucible at 600 °C for 15 s, with a heating rate of 20 °C ms^{-1} and the interface maintained at 260 °C. The pyrolyzes were purged from the interface into the GC injector under inert conditions using helium gas. The identification of the pyrolysis products was made using an MS instrument (Agilent Techs. Inc. 6890 GC / 5973 MSD) with HP-5MS ((5%phenyl)-methylpolysiloxane) column (30 m ×

0.25 mm x 0.25 μm). The obtained mass spectra were compared with the National Institute of Standards Library (NIST) and with compounds reported in the literature.

2.3.6 Total phenolic content

The total phenolic content (TPC) of lignin samples was determined by the Folin–Ciocalteau spectrophotometric method using Gallic acid as a reference compound and dimethyl sulfoxide (DMSO) as a solvent. As the first step, a calibration curve was calculated with six different concentrations (100–1000 mg L^{-1}). Lignin samples were dissolved in DMSO (2 g L^{-1}). For the analysis, 0.5 mL of lignin solution, 2.5 mL of Folin–Ciolcalteau reagent, and 5 mL of Na_2CO_3 (200 g L^{-1}) were added to 50 mL volumetric flask and covered with distilled water. The samples were kept in a thermostatic bath at 40 °C for 30 min before measuring the photo-spectral absorbance at 750 nm (Jasco V-630 spectrophotometer). The blank was prepared in the same way but adding 0.5 mL of DMSO instead of the sample. The total phenolic content of lignin samples was expressed as Gallic acid equivalents (mg GAE per g lignin). Both parameters were calculated on a dry basis.

$$GAE = 100 \times C_{GAE}/C_{sample} \times [1-(H)/100]$$

Where C_{GAE} is the concentration of Gallic acid obtained by the calibration curve, C_{sample} is the concentration of the lignin sample in DMSO (expressed as mg L^{-1}), and H is the humidity content.

2.3.7 Molar sizes of the obtained lignins

The comparison of the molar size of the different lignin samples was developed by determining the mass average molar mass (Mw) and the polydispersity index (Mw Mn^{-1}) using gel permeation chromatography (GPC). For this, a Jasco LC-NetII/ADC chromatographer equipped with a reflection index detector was used, using a PolarGel-M

guard (50 mm 7.5 mm) and two PolarGel-M columns in series (300 mm 7.5 mm). The samples were analyzed with dimethylformamide as a mobile phase with 0.1% lithium bromide; the flow rate was set at 0.7 mL min^{-1} and temperature at 40 °C. The calibration was carried out using polystyrene standards (Sigma-Aldrich), ranging from 266 to 70,000 g mol^{-1}.

2.3.9 Thermal analysis of lignins

A Thermogravimetric Analysis (TGA) was carried out to determine the thermal transitions and the thermal stability of the lignins. This characterization was carried out in a TGA Q2500 calorimeter from TA, with a heating ramp of 10 °C min^{-1}, from 30 to 800 °C in a controlled N_2 atmosphere.

3. Results and Discussion

3.1 Organosolv pre-treatment

Figure 1 shows the values of the characterization of the raw material. Although all the woods used were hardwoods and the cellulose contents are similar, in the case of lignin, it can be seen that there are considerable differences. The highest content of lignin is found in Northern red oak (NRO) and black locust (BL), while Iberian white birch (IWB) and common ash (CA) have values lower than 15%.Hhowever, these values correspond to the average lignin content of hardwoods. The hemicelluloses content ranges between 18.60 % (BL) and 30.77 % (IWB). Iberian white birch, common oak (CO), and sweet chestnut (SC) have the highest content; these values are within the typical values for hardwoods, as reported by Saidur et al. [29]. Ethanol-toluene extractives were between 2.08% (IWB) and 7.18% (BL). Iberian white birch has the lowest extractive content (2.08%), while black locust has the highest (7.18%) with values similar to those of literature [30, 31]. Regarding lignin content, there are clear differences between the selected wood species, not only for AIL but also for ASL, where the highest value is reached

by Northern red oak. Black locust has one of the highest measured AIL and total lignin content, only behind Northern red oak. Black locust also has the lowest hemicellulose content, which facilitates lignin extraction, obtaining the highest AIL (89%). This high content of AIL in black locust is consistent with the work by Chow et al. [32]. Table S1 in the supplementary information presents the full values for each component.

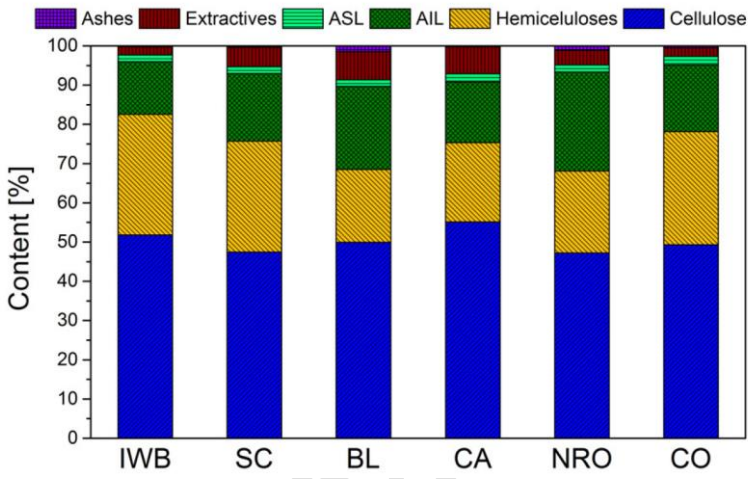


Figure 1. Chemical composition of the different raw materials.

Table 1 presents the different yields from the Organosolv treatment. The higher yield of delignified solid was of Iberian white birch, which had around 10% more than the average. The rest of the delignified solids averaged 52.85 grams per 100 grams of raw material. On the other hand, the recovered black liquors averaged 72.36 mL per each 100 mL of white liquor; this means that the swelling of the delignified fibers was around 28 mL per each 10 g of fibers. No significant differences were observed in the black liquor yields for the different species. However, in terms of the content of organic matter in liquor, common oak had 4.17 grams per 100 mL; this is 10% over the average organic matter content of the other species. On the other hand, Iberian white birch and common ash had 5% less black liquor content than the average. In Figure S1 in the Supporting Information, the lignin content decreased considerably in the composition of the delignified solid by increasing the glucan and

hemicellulose content. Common ash pulp was the one with the highest lignin removal. By comparing results from Table 1 with those presented in Figure 1 and Figure S2 in the Supporting Information, it can be seen that the lower yields, which correspond to NRO and SC, are consistent with the lowest cellulose contents, which means that the Organosolv treatment was efficient in extracting lignin.

Moreover, the highest yields correspond to IWB, BL, and CO; these are also cellulose-rich raw materials. The sample presenting an off-the-trend result is common ash, which has the highest cellulose content and the second lowest lignin content. This can be related to the formation of lignin-carbohydrate complexes or with more condensed lignins presenting recalcitrance to the treatment, regardless of its content.

Table 1. Yield of Organosolv treatments.

	IWB	**SC**	**BL**	**CA**	**NRO**	**CO**
Delignified solid[1]	60.93	47.34	54.21	51.95	50.17	52.5
Organosolv liquor[2]	71.27	72.03	74.71	73.57	73.82	68.75
Organic matter in liquor[3]	3.59	3.78	3.84	3.59	3.70	4.17
Inorganic matter in liquor[3]	0.04	0.04	0.03	0.06	0.03	0.02

[1] Relative yield: total recovered mass in g per 100 g of dry raw material.

[2] Relative yield: total recovered black liquor in mL per 100 mL of white liquor.

[3] Relative yield: total recovered mass in g per 100 mL of black liquor.

3.2 Cellulose fraction

Table 2 shows the percentage of solid recovered after each stage. After ECF bleaching, which consists of bleaching with sodium chlorite, there is a recovery of between 75 and 78% of solid matter.Tthis occurs because said bleaching removes residual lignins from the fibers, which are degraded by sodium chlorite. The mass loss between stage 1 and stage 2 is due to the residual

lignins oxidized by hydrogen peroxide and, to a lesser extent, to some degraded polysaccharide by the action of the alkaline medium (sodium hydroxide) [33]. Moreover, the cellulose contents from the bleached pulps, ranged between 73 and 80 %, with most of them near 80%. Iberian white birch had the lowest yield of recovered cellulose compared to the original content of the raw materials, as shown in Figure 1.

Table 2. Yields and purity of the bleached pulp.

	Units	IWB	SC	BL	CA	NRO	CO
Bleaching stage 1[1]	[g]	79.93	84.57	86.06	88.56	85.00	83.27
Bleaching stage 2[1]	[g]	99.80	98.62	97.93	94.56	90.60	93.91
Total bleached pulp[2]	[g]	48.60	39.48	40.79	43.50	38.70	40.79
Cellulose in pulp[3]	[%]	73.74	78.99	80.64	78.20	79.54	77.61

[1] Process yield: solid recovered after process per 100 g of input biomass.

[2] Relative yield: total recovered mass per 100 g of dry raw material.

[3] Pure components content.

Figure 2 shows the simulated color changes throughout the delignification and bleaching; CIELab coordinates can be consulted in Figure S2 at the Supporting Information. From the color analysis, most of the bleached pulps have lightness between 91 and 95, with Iberian white birch as the one achieving the whitest color. An increase on the darkness with low reduction of a* and b* for all Organosolv delignified solids (ODS) and is related to polyphenolic chromophores originated from the ring-opening of lignin chains [24], this was more pronounced in black locust and sweet chestnut, while the lowest darkening occurred to common ash. However, this had no particular influence in the lightness of their bleached pulps. After the Iberian white birch, common ash and sweet chestnut presented the highest lightness values.

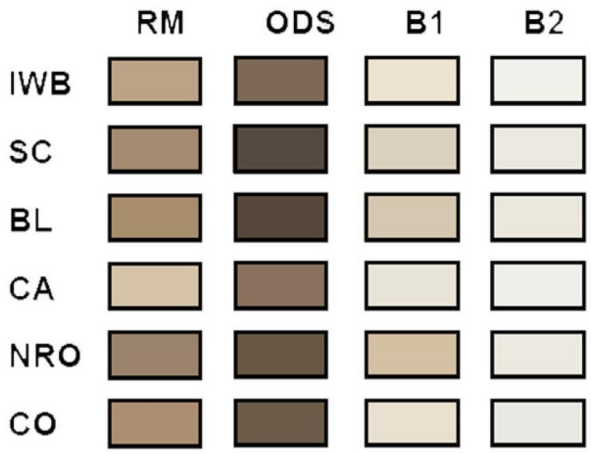


Figure 2. Color changes of the different pulps.

Figure 3 shows the bands corresponding to the spectra of the celluloses. In them, a wide band between 3500 and 3000 cm^{-1} can be observed, which corresponds to the free -OH that are found in the cellulose molecule and which are fundamental when granting specific functionalities to the cellulose by means of reactions of chemical modification of the surface. In this region, the weaker OH band is that of NRO, which might be related to the age of the sample. The bands at 3000-2800 cm^{-1} are attributed to CH stretching vibrations; in this region, the samples containing more intense signals are NRO and SC, while CO and IWB resulted in the weakest. The bands at 1375, 1240, 1165, 1060 1030 are assigned to characteristic CO, C–H, C–O–C, C−O deformation or stretching vibrations of different groups from carbohydrates [34]. In this range, little differences can be seen between samples, these differences being the main aspects of the weaker C-H and C-O-C bands for NRO and BL, as well as the stronger C−O bands of CO and IWB.

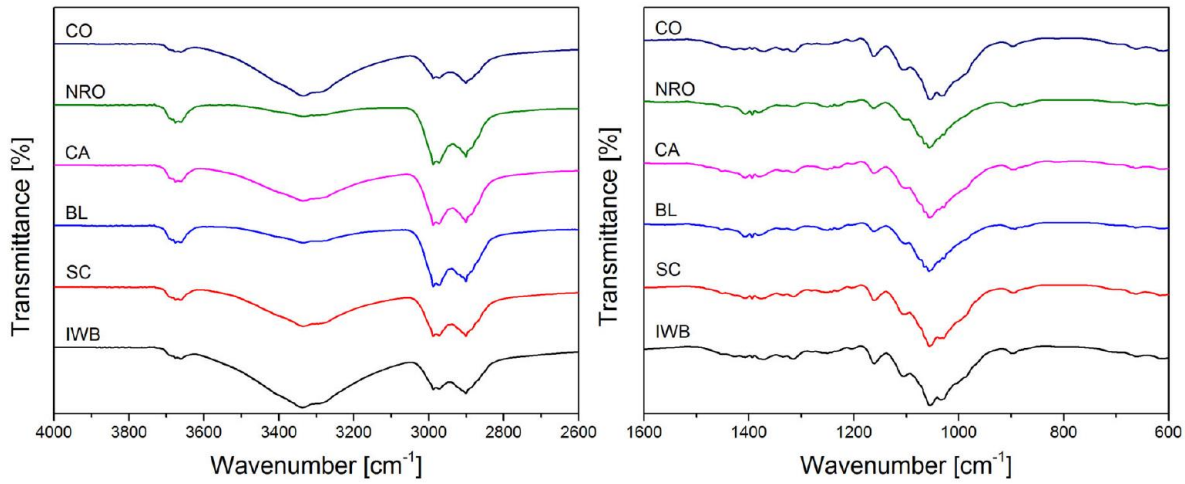


Figure 3. Infrared spectra of the obtained celluloses.

The X-ray patterns of the different samples are presented in Figure 4. In them, a more significant similarity in the morphology of the signal diffracted at 2θ 20-25 can be highlighted, which corresponds to the plane 200 present in cellulose Iβ, which are the most abundant in native plants. The widening or narrowing of the said region is closely related to the size of the crystalline domains of the samples, the broadest being those that have a smaller size. Black locust is the species that presents the most considerable narrowing in that region, which can be explained by the presence of more significant crystalline domains [35]. In general, the celluloses obtained by Organosolv treatment have high crystallinity because of the removal of less ordered carbohydrates. The cellulose with less crystallinity is that of common oak (73.59%), which may be related to the original state of the biomass or the residual presence of less ordered carbohydrates. The highest crystallinity is that of black locust (86.31%), which also corresponds to the highest content of pure cellulose, as shown in Table 2, thus meaning that black locust has the cellulose with the best quality. The rest of the crystallinities are within the same range, 78.67% for Iberian white birch, 78.11% for the sweet chestnut, 76.93% for common ash, and 77.90% for Northern red oak. These values are high

compared to other Segal CI [36] but the reason for that is the efficiency of the selected pulping and bleaching sequences.

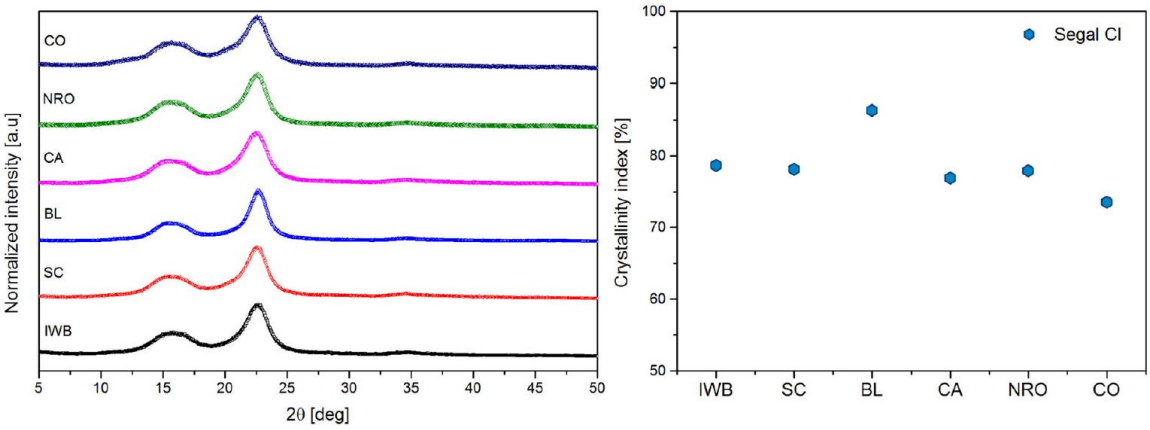


Figure 4. XRD diffraction patterns and Segal CI of the obtained celluloses.

In Figure 5, AFM images of different obtained nanofibers are displayed. As can be seen, unitary fibrils do not present significant differences between each other at the nanoscale. The main aspects occurred during the fibrillation process. Figure S3 in the Supporting Information shows further information regarding the defibrillation of the bleached pulps through HPH. In Figure SA and B in the Supporting Information, one of the main issues during defibrillation can be identified, which correspond to unfibrillated fibers of sweet chestnut (S3 A) and common ash (S3 B). In Supporting Information Figure S3 C (black locust), D (Iberian white birch), and F (common ash) another issue can be observed, which is the entanglement of already fibrillated CNF, this type of entanglement does not represent an issue for specific applications (additive, nanopaper, etc.) but can pose severe problems for other (reinforcement in polymer matrix, surface modification, etc.). In general, size ranges tend to be similar, with a 48.73 nm mean diameter and lengths varying significantly in each sample but with no relevant difference between the used species as can be seen in both Figure 5 and Figure S3 in the Supporting Information, in which S3G corresponds to common oak, H to Northern red oak, and I to the sweet chestnut.

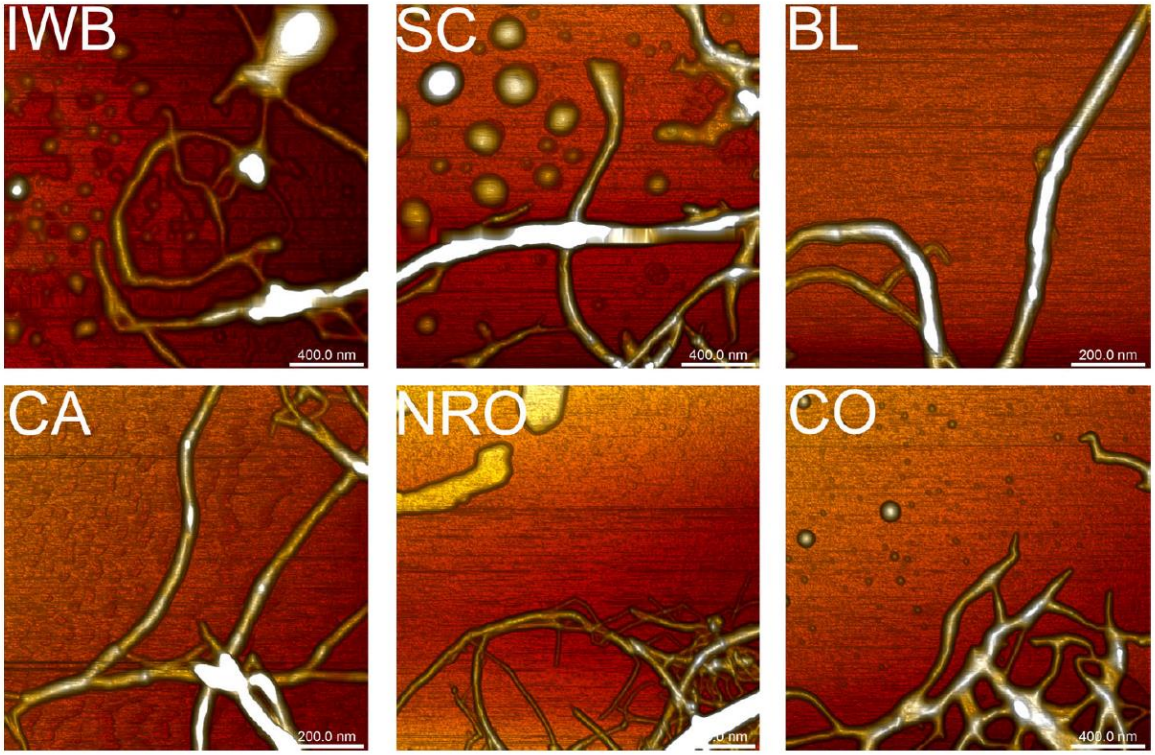


Figure 5. AFM images of individual CNF obtained from the different hardwood species.

3.3 Lignin fraction

Table 3 presents the purity of the different lignins in terms of AIL content; most of them are lignins of high purity, as the overall AIL is above 80%. All the obtained values are higher than those reported by Sequerios and Erdocia for lignin purity of Organosolv and formosolv of olive tree pruning, respectively [37, 38]. Black locust lignin is the one with the highest AIL, while Northern red oak is the one with the lowest. The high AIL content is due to the extraction process (Organosolv), which is, in general, less aggressive towards lignin, resulting in lignin of higher quality. The values of ASL content are between 2 and 4%, which is similar to data reported previously for other Organosolv hardwoods [37, 38]. Lignin is also linked to hemicelluloses forming lignin-carbohydrate complexes (LCC), these impurities in lignin can be quantified by measuring the sugar content of the samples. These LCC can be extracted and dissolved along with lignin and hemicelluloses in the spent liquors [39, 40]. In the analyzed samples, the carbohydrate content in lignins was between 3 (Northern red oak and common

oak) up to ~10 (black locust). The carbohydrate content of lignins, while relatively high, is in accordance with other Organosolv lignins produced from different hardwoods under diverse conditions [11]. The total phenolic content was carried out to obtain the content of phenolic hydroxyl groups on the lignins, whihc is related to the reactivity of lignin to potential functionalization or its compatibility with polymer blends. The procedure used for that was the Folin-Ciocalteau as it is fast and can easily be compared with literature. that the phenolic group content of the lignins varies according to the tree species. The lignin with the morst phenolic OH groups is common oak, followed by sweet chestnut, both surpassing 40 mg of GAE per gram of lignin. Black locust, common ash, and Iberian white birch obtained values around 30 mg of GAE per gram of lignin, and they are in the same range that the values reported for Eucalyptus Organosolv lignin by Gordobil [41], while the phenolic content of Northern red oak lignin is the lowest.

Table 3. Lignin yields and qualitative assessment.

	Units	**IWB**	**SC**	**BL**	**CA**	**NRO**	**CO**
Lignin[1]	[g]	15.52	17.90	18.80	14.39	16.40	18.19
Acid insoluble lignin[2]	[%]	82.55	83.04	89.23	84.43	81.70	86.01
Acid soluble lignin[2]	[%]	2.16	3.23	2.44	2.45	3.26	3.91
Carbohydrates[2]	[%]	6.91	5.65	9.80	5.02	3.14	3.24
GAE[2]	[mg g^{-1}]	30.36	40.61	33.86	31.09	26.76	42.43
Ashes[2]	[%]	1.05	1.05	0.75	1.60	0.89	0.50

[1] Relative yield: total recovered mass per 100 g of dry raw material.

[2] Pure components content.

The infrared spectra (FT-IR) of the lignins obtained by Organosolv treatment are presented in Figure 6a. A broad band with low intensity in the region of 3700-3000 cm^{-1} can be noticed,

which corresponds to the phenolic hydroxyl groups (-OH) of lignins. A narrower band in the 2900 cm^{-1} region, generally attributed to the methoxy groups that are characteristic of hardwood lignins, is also seem in all samples, presenting higher intensity in case of common oak lignin. Residual esters from lignin-carbohydrate complexes can be seen in the band between 1700-1710 cm^{-1}, more visible in case of sweet chestnut and Northern red oak than in the rest [42]. In the region of 1595 and 1510 cm^{-1}, there are two bands corresponding to the C-C of aromatic skeletal ring vibrations in lignin. Aromatic skeletal vibrations combined with C–H in the plane of lignin can be observed at the 1460 cm^{-1} band, which can overlap also with those of LCC. The band at 1325 cm^{-1} can be attributed to the presence of syringyl units (C-O stretch). Bands marked at 1220 cm^{-1} (C-C), 1125 cm^{-1} (C-O), and 1030 cm^{-1} (C-O) of guaiacyl and syringyl units in hardwood lignin [12].

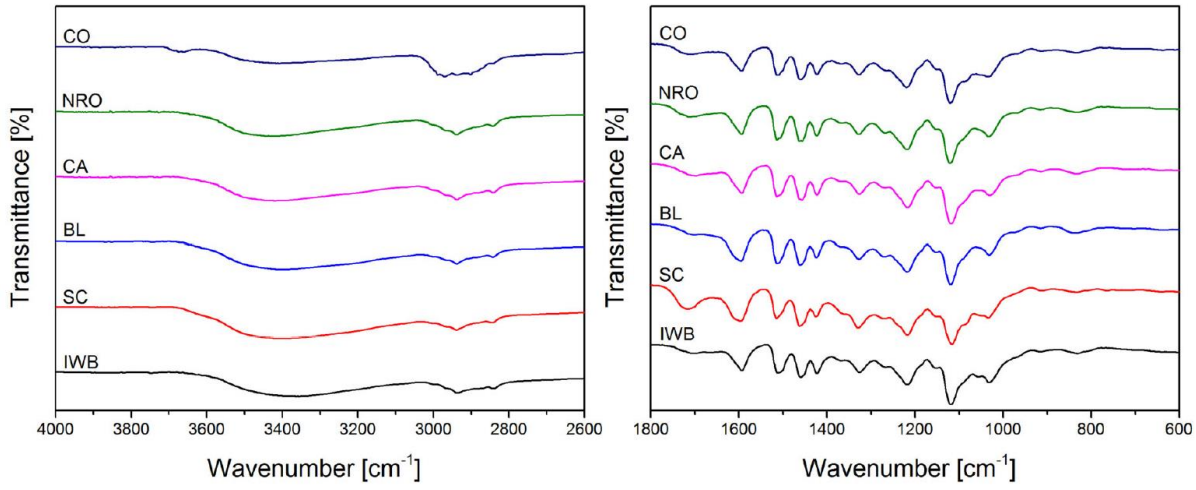


Figure 6. Infrared spectra of the obtained lignins.

In terms of quality, hardwood lignins are composed mainly of syringyl (S) and guaiacyl (G) units, with a minor amount of p-hydroxyphenyl (H). Table S3 in the Supporting Information presents a summary of the compounds identified by Py GC-MS and their contribution to the total mass of lignin and the group S (syringyl) or G (guaiacyl) to which they belong. The proportions m/z (mass/charge) are also presented, which relates the molecular mass of the

compound with its charge [12, 43, 44]. In general, the S/G ratios (Table 4) of the analyzed species reveal typical hardwood S/G ratios, ranging from 1.86 up to 2. The S/G ratio ranges are in agreement with values obtained by Erdocia et al. (acetosolv lignin 2.05; formosolv lignin 1.96 and acetosolv-formosolv lignin 2.01) for Olive tree pruning lignin[38].

Table 4. Lignin S/G ratio of the different species.

	IWB	**SC**	**BL**	**CA**	**NRO**	**CO**
Total S	64.62	63.42	62.75	62.06	63.68	61.01
Total G	32.44	32.50	33.31	33.87	31.82	32.86
S/G ratio	1.99	1.95	1.88	1.83	2.00	1.86

One of the essential characteristics of lignin is the average molecular weight, which is presented in Figure 7. Since different factors may influence the determination of lignin molar mass using GPC [45], the presented results intend to provide a semi-quantitative analysis of the extracted lignins and to verify tendencies with cross-validation using Py-GC/MS. Low molecular weight lignins are more recalcitrant for pulping; however, once obtained are suitable for depolymerization or to elaborate polymer blends [46]. Considering that lignin has non-uniform chains, molecular weight is expressed as an average, as seen in Figure 7.Tthe retention time of size-exclusion chromatography shows broad molecular weight distributions. In general average molecular weight (Mw) ranged between 5000 and 7500 g mol^{-1}; these molecular weights can be considered low-medium, as lignin molecular weight can be from 1000 up to 80 000 g mol^{-1} [47]. Polydispersity (Mw Mn^{-1}) ranged from 5.1 to 6.3, which is considered high value, this is generally due to the conditions of Organosolv treatment leading to different rates of repolymerization after extraction [48]. This can be corroborated by the relationship between Mw and the S/G ratio, as a higher content of S units leads to larger

lignin polymerization fragments, which is demonstrated by a positive correlation between Mw and lignin S/G ratio [49]. Most of the lignins follow this argument, having a Pearson coefficient of 0.26; however, if sweet chestnut lignin is not considered, the correlation coefficient is raised to 0.59.

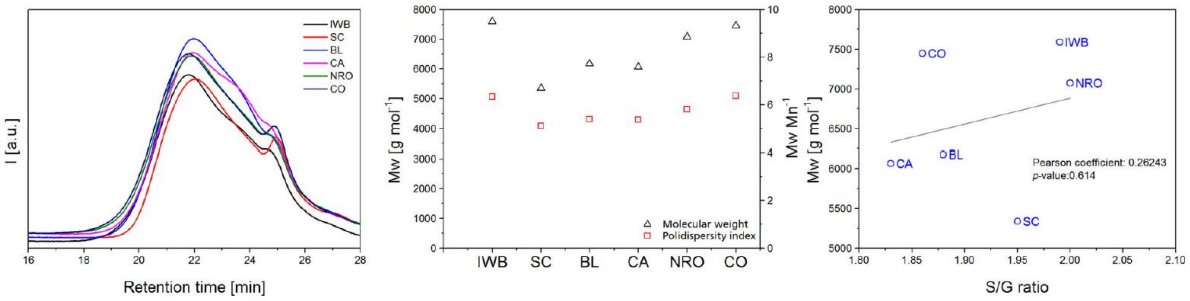


Figure 7. GPC retention time diagrams, mass average molar mass (Mw), polydispersity index (Mw Mn^{-1}), and the correlation between S/G ratio and molecular weight of the obtained lignins.

Thermogravimetric analysis in an inert atmosphere (N_2) was used to evaluate the pyrolytic behavior of lignins. Figure 8 shows the thermograms of Organosolv lignins, the dTG (inset), as well as the final residue and the temperatures at which 5% and 50% degradation are achieved. In these graphs, it can be observed that the lignin having the highest thermal stability is that of sweet chestnut, which maintains a higher resistance to degradation (≈200 °C more than the rest). Furthermore, sweet chestnut lignin is also the one that presents the highest amount of residue (41.7%). On the other hand, the lignins of the Quercus family (Northern red oak and common oak) are the ones having the least resistance to thermal degradation, being the first ones to initiate their degradation (low $T_{5\%}$). The $T_{50\%}$ is related to the thermal stability of the lignin; in this sense, the sweet chestnut was the most stable as it has a higher $T_{50\%}$. Another important aspect of this analysis is the temperature of maximum degradation, in this case, the sweet chestnut and black locust lignins stand out, having a lower T_{max}, while the lignin with higher T_{max} is the common oak. These data are concurrent with

those obtained from molecular weight and polydispersity since a curve of thermal degradation with steeper slope (and therefore with greater width in the curve of the derivative) is closely related to a higher polydispersity [50], which is visible in the case of common oak and Iberian white birch (high molecular weight) and sweet chestnut (low molecular weight). This effect takes place since lignins with lower molecular weight tend to volatilize more quickly once the degradation temperature has been reached. Final residue consisting of char presented higher values in sweet chestnut, black locust, and Northern red oak; higher yield of char is related to the presence of aromatic rings in the pyrolytic biomass [50].

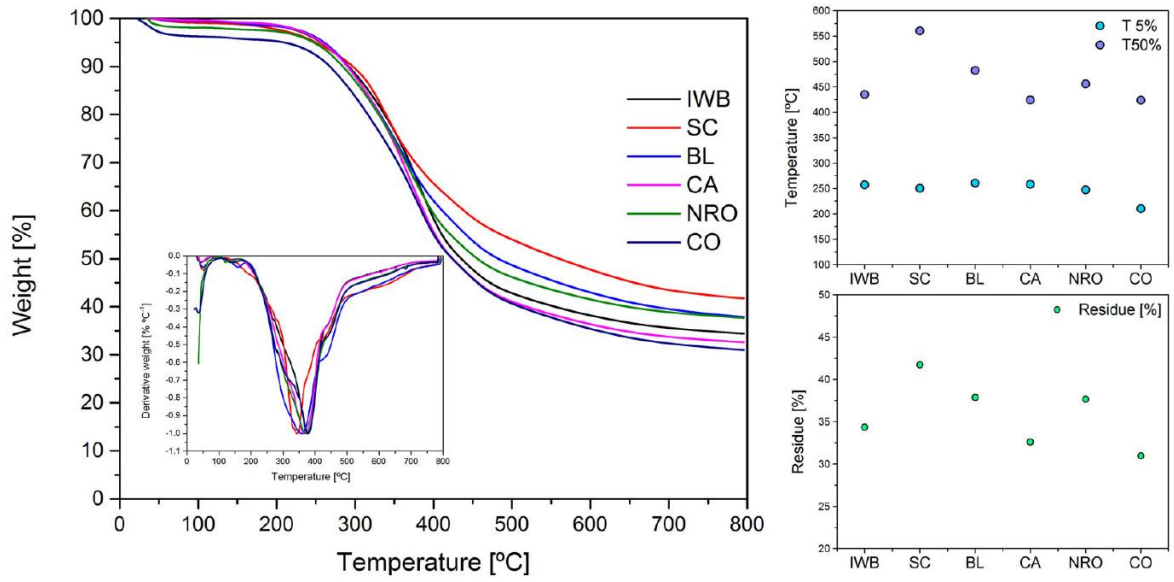


Figure 8. TGA thermograms, transition temperatures, and final residues of the obtained lignins.

4. Conclusions

Six different wood species were characterized and fractionated to provide an alternative to the traditional management of the Atlantic mixed forest. Evaluating the potential exploitation of byproducts during the growth of the trees will promote the care and cleaning of the forest. Chemical composition of wood showed similar cellulose content; however, there are significant differences in the extractives, lignin, and hemicellulose content. Regarding quality

and potential valorization, Organosolv lignin from sweet chestnut is distinguished and has a lower molecular weight, which makes it attractive for the depolymerization of lignin in high value-added fractions. Moreover, the resulting bleached black locust pulp had the highest quality, being the one with the highest content of cellulose, which also had the highest crystallinity. However, the resulting defibrillated CNF had a better aspect ratio for Northern red oak and common oak, while for sweet chestnut and common ash, the defibrillation resulted in lower quality CNF. In terms of global recovery, Iberian white birch had the highest pulp and lignin recovery, with a total amount of 64.12 grams of products per every 100 grams of raw material; nevertheless, the purity of both was the lowest among the analyzed raw materials. Concerning the nano-scale, the differences between the obtained cellulose nanofibers were minimal. In general, the assessment of yields and properties of the recovered products makes the use of clear-cutting and pruning residues from Atlantic mixed forest a suitable source of value-added products through the biorefinery valorization concept. The similitudes between the obtained products would make an Organosolv treatment of the different raw materials in the same process possible, which would allow a comprehensive valorization of all the wood species with the potential economic benefits.

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