WOOD2WOOD

A Wood-to-Wood Cascade Upcycling Valorisation Approach

» Deliverable 7.1

Cascade to function, mixed wood treatment

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GLOSSARY OF ACRONYMS

Acronym	Extended definition
AFM	Atomic force microscopy
AIL	Acid insoluble lignin
ASL	Acid soluble lignin
C&D	Construction and Demolition
CNF	Bleached cellulose nanofibers
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetry
FB	Fibreboard
FTIR	Fourier-transform infrared spectroscopy
LCC	Lignin-carbohydrate complexes
LCNF	Lignocellulosic nanofibers
MRM	Mixed raw materials
MW	Mixed softwoods
OCNF	Organosolv cellulose nanofibers (bleached)
OLCNF	Organosolv Lignocellulose nanofibers
OP	ORGANOSOLV pulp
PB	Particleboard
PDI	Polydispersity index
PLA	Polylactic acid
SEC	Size exclusion chromatography
SL	SODA lignin
SP	SODA pulp
TAPPI	Technical Association of the Pulp and Paper Industry
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
^{13}C NMR	Carbon-13 Nuclear magnetic resonance
^{31}P NMR	Phosphorus-31 Nuclear magnetic resonance

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EXECUTIVE SUMMARY

Task 7.1 is focused on the production of fillers from waste wood to enhance the durability and performance of the PLA- biocomposites. The results showed the feasibility of obtaining nanofillers (cellulose nanofibers and lignin) from waste wood. The main achievements of this Task are summarised below:

i. The different fractions of waste wood (Particleboard (PB), Fibreboard (FB), Mixed Softwoods (MW)) were chemically characterised, and a blend of the different fractions was selected for fractionation.
ii. Three delignification methods (organosolv, Acetoformosolv and Soda) were performed. Acetoformosolv (AP) and Organopulp (OP) yielded the best results, offering high cellulose and lignin recovery, while Soda pulping was less effective due to cellulose degradation and high inorganic content.
iii. Bleached cellulose nanofibers (CNF) and Lignocellulosic nanofibers (LCNF) were successfully produced by mechanical homogenization using bleached and unbleached organosolv pulp. LCNF produced from the unbleached organosolv pulp (OLCNF) showed optimal morphology and good thermal stability.
iv. The OLCNFs were chemically modified through esterification and silanization, making them ideal for PLA composite reinforcement.
v. Lignins obtained by precipitation from the three deglinification processes were characterised. The results showed that lignins from OP treatment (OLF) displayed superior purity, structural properties, and thermal behaviour.
vi. The fatty acid esterification of the Organosolv lignin (OLF), enhanced its hydrophobicity and processability, despite a slight drop in thermal resistance.
vii. Ultimately, both OLCNF and OLF were selected as the most promising cellulose and lignin components for PLA-based composites.

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1. INTRODUCTION

The European Environment Agency (EEA) emphasizes that Europe and the world are confronting unprecedented sustainability challenges, including climate change, biodiversity loss, resource depletion, and pollution. These issues are predominantly driven by unsustainable consumption patterns, as countries strive for economic growth and people pursue well-being, which in turn increases environmental pressures and accelerates climate change (European Environment Agency, 2023). As a response to these challenges, sustainable resource management and innovative waste valorization strategies have gained significant attention. Among these, the valorization of biomass residues has emerged as a key approach to advancing the circular economy, providing a sustainable solution to mitigate environmental degradation and promote resource efficiency (Ahmed et al., 2021; Ghobadi and Sepasgozar, 2023). One of the most promising strategies for resource recovery is recycling waste wood, which serves as a significant yet underutilized source of lignocellulosic biomass. Unlike traditional reliance on virgin timber, which contributes to deforestation, habitat destruction and carbon emissions, waste wood recycling offers an environmentally friendly alternative.

The W2W project, aligned with the EU's sustainability agenda, focuses on the valorisation of recycled wood derived specifically from the Construction and Demolition (C&D) sector which represents a largely untapped yet abundant source of lignocellulosic biomass. In response to the growing pressure on natural resources and the predicted shortfall in wood supply by 2030 (Höglmeier et al., 2014), W2W aims to develop innovative pathways for reprocessing C&D wood waste into valuable materials. By targeting this waste stream, the project contributes directly to the circular economy, reducing reliance on virgin timber, curbing deforestation, and lowering carbon emissions. Through sustainable resource management and advanced recycling strategies, W2W demonstrates how rethinking waste from the built environment can significantly support Europe's transition toward a more resource-efficient and climate-resilient future.

Lignocellulosic biomass is composed primarily of cellulose, hemicellulose, and lignin is a renewable and abundant resource with significant valorization potential. Cellulose, the most abundant biopolymer on Earth, is widely utilized in paper, textiles, and biofuel industries. Recent advancements have expanded its applications, including cellulose nanofibers for aerogels and hydrogels. Similarly, lignin, a complex aromatic polymer, has applications in adhesives, bio-polyols production, and other bio-based chemicals. Despite these advantages, the efficient extraction and separation of these components from waste wood remains a challenge, necessitating optimized fractionation methods.

Task 7.1 focuses on the valorisation of waste wood through its conversion into cellulose nanofibers and lignin *via* fractionation processes, aiming for their integration into PLA-based composites. The work begins with the characterization of the raw materials, followed by the application of various fractionation techniques to identify the most suitable method. This selection is based on the detailed characterization of both delignified pulps and the extracted lignins. The resulting pulps are then subjected to nanofibrillation to assess the quality of the produced nanofibers and identify the optimal option. Additionally, bleached pulps are also obtained to determine whether bleaching is necessary. In the final phase, modification processes are applied to both lignin and nanocellulose to enhance their compatibility and performance within the PLA composite matrix. The workflow of Task 7.1 is represented in **Figure 1**.

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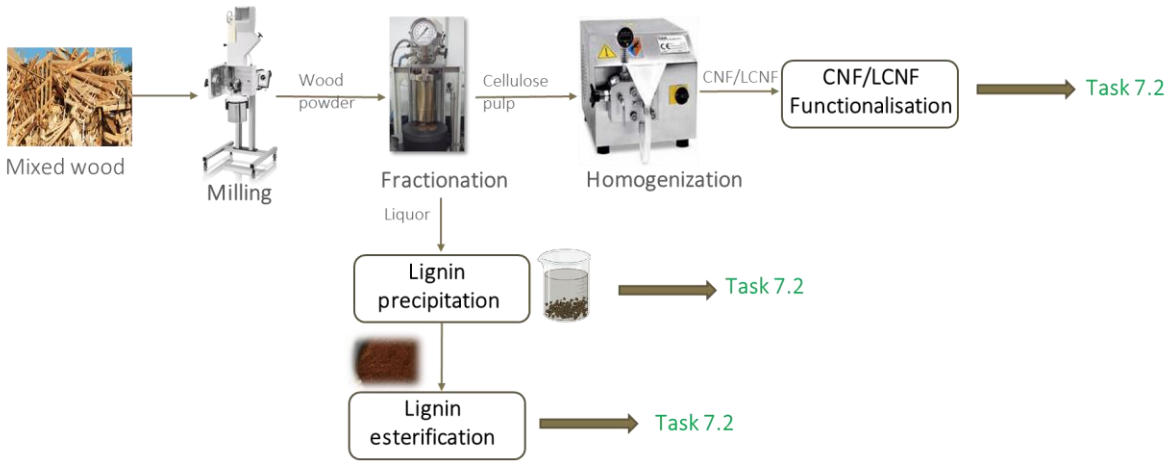

Figure 1 Workflow of the Task 7.1

2. EXPERIMENTAL METHODS

The characterization of raw materials is an essential process for understanding their composition and behavior, especially when evaluating their suitability for specific applications. In this study, we investigated the potential of waste wood from the construction and demolition (C&D) sector, with a particular focus on the various physical and chemical properties that influence subsequent processing. Prior to characterization, a comprehensive pretreatment process was conducted, which involved the separation of bulk contaminants, followed by sorting the wood into distinct categories. Further processing steps regarding pretreatment were discussed here. Characterization of the raw materials was performed following TAPPI standards, which are recognized for their reliability in assessing the composition and quality of lignocellulosic materials, including moisture content, ash content, solvent extractives, and holocellulose and α-cellulose. Additional analyses, including Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA), were employed to further investigate the chemical, structural, and thermal properties of the raw materials. These analytical methods provided valuable insights into the composition and behavior of raw materials, cellulose and lignin ultimately aiding in the selection of suitable processing pathways for the development of high-quality end products.

2.1. RAW MATERIALS

The characterization of raw materials is a crucial step in understanding their composition and behaviour, particularly when evaluating their potential for various applications. In this study, raw materials were analysed to assess their suitability for further processing. Before the characterization, a pretreatment process was applied to raw materials. This pretreatment involved separating bulk contaminants, followed by sorting the wood into different categories. The sorted materials were shredded, ground, and homogenized to prepare the samples for detailed characterization. The characterization process itself involves determining key properties such as moisture content, ash content, solvent extractives, and the chemical composition of holocellulose and cellulose. These characteristics are important as they influence the efficiency of subsequent processing steps and the quality of the final product.

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2.1.1. Pretreatment

The waste wood from C&D sector was provided by Ecomaison (France), which did not have any prior chemical pretreatment. First, bulk contamination, which involved metallic fasteners, metallic reinforcement layers, and fiberglass, was separated from the wood waste. Then it was observed that the wood residue received presented certain level of heterogeneity, and therefore it was sorted into different categories: natural wood which is mainly mixed softwood (MW), and synthetic wood which was subsequently divided into two fractions labelled as particle board (PB) and fibreboard (FB), as illustrated in **Figure 2**. The different wood categories were shredded separately in a wood crusher and then ground and homogenized using Retsch Hammer mill 2000 into particle sizes 2.5-4 mm according to standard methods of the Technical Association of the Pulp and Paper Industry (TAPPI, T257-cm85). It should be mentioned as well that coatings and glues, which were present in the fraction of the synthetic wood, were kept and shredded with the wood as removing those contaminates is a big obstacle that makes the recycling process more challenging.

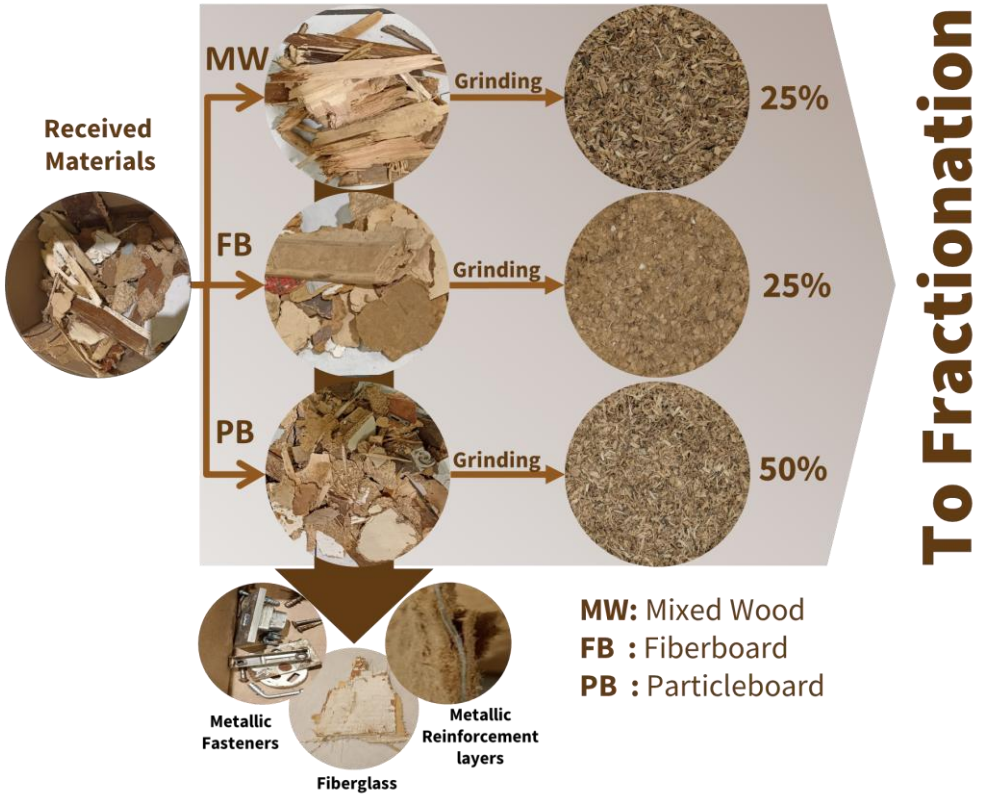

Figure 2. Raw Material Identification.

2.1.2. Characterization of raw materials and delignified pulps

For characterization of the raw materials TAPPI standards was followed. TAPPI provides standardized methods for characterizing the composition and thermal properties of lignocellulosic materials, including the measurement of cellulose, lignin, hemicellulose, extractives, and inorganic content. TAPPI measurement was followed by a group of structural analyses.

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2.2. FRACTIONATION AND PRECIPITATION OF LIGNINS

A mixture of various categories of waste wood (MRM) was subjected to fractionation using three different delignification methods.

2.2.1. Acidic delignification

Acidic delignification was carried out using a solution of Acetic acid/Formic acid/water (60/30/10, v/v/v) in an autoclave at 121 °C for 90 min with a solid-to-liquid ratio of 1:10 (% w/w) and 0.2%wt of HCl as a catalyst (Erdocia et al., 2014a). After separating ACETOFORMOSOLV pulp (AP) from the black liquor, 5 volumes of water were added for pursuing the precipitation of the lignin. Alkaline delignification.

Alkaline (SODA) delignification was carried out in borosilicate glass using sodium hydroxide solution (7.5%wt.) with solid-to-liquid relation 1:6 (w/v) in an autoclave at 121 °C for 90 min (Morales et al., 2020a). After the delignification process was completed, the suspensions obtained were filtered to separate the pulp and the liquors. Then, the lignin was precipitated from this liquor by adding 2 volumes of acidified water (H_2SO_4) at pH~2 .

2.2.2. Organosolv delignification

Organosolv delignification was performed using a dissolution of 70/30 EtOH/water (v/v) at 200 °C and 90 min with constant stirring and solid-to-liquid relation 1:6 (w/v) in a 1.5 L stainless steel 5100 Parr reactor (Fernández-Rodríguez et al., 2021). After the delignification process, the pulp and the black liquor were separated. Then the black liquor was added to volumes of acidified water (H_2SO_4) at pH~2 and it was left precipitating for 24 h (de Hoyos-Martínez et al., 2018). The obtained lignin was then filtered and dried.

2.3. CELLULOSE FRACTION

Based on the pulps obtained from the different delignification processes described in the previous section, lignocellulosic nanofibers (LCNF) were produced by mechanical defibrillation.

Additionally, the most promising pulp from one of the delignification routes was subjected to a bleaching treatment to remove residual lignin and obtain a purified cellulose pulp. The bleaching was conducted using a reflux set-up, in an oil bath at 75 °C for 4 h, employing an aqueous mixture of acetic acid and sodium chlorite. This bleached pulp was then mechanically defibrillated to produce cellulose nanofibers (CNF), which were also subjected to surface functionalization. Two distinct strategies were applied for both LCNF and CNF: silanization, and esterification. These modifications aimed to introduce functional groups onto the nanofiber surfaces to enhance the interfacial bonding between the nanofibers, lignin and the polylactic acid (PLA) polymer matrix in the final composite materials.

2.3.1. Isolation of cellulose nanofibers (CNF)

From the pulp obtained after delignification, lignocellulose/cellulose nanofibers were extracted. To achieve this, the wet pulps were first dispersed in water. The dispersion was then subjected to high-shear homogenization using an Ultraturrax device. Subsequently, the fibers underwent mechanical defibrillation with a GEA Niro Soavi high-pressure homogenizer.

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2.3.2. Functionalization of cellulose nanofibers

Two modifications were performed. *LCNF/CNF* were chemically modified with silane. For the esterification, carboxylic acid was used. The modified LCNF/CNF were characterized using different techniques: FTIR, NMR, DSC, TGA, AFM, XRD and water contact angle.

2.4. LIGNIN FRACTION

In this section the analysis of the lignins extracted, as well as, the process of chemical modification and the subsequent assessment, are presented.

2.4.1. Lignin chemical composition

Different physicochemical parameters of lignin were analysed to elucidate its composition and purity. Thereby, acid insoluble lignin (AIL), acid soluble lignin (ASL), lignin carbohydrate complexes (LCC) and inorganic compound contents were determined.

2.4.2. Lignin modification

The lignin chemical modification had the purpose of introducing ester groups into its structure and with this aim fatty acid was used as main reagent.

2.4.3. Lignin characterization

The lignins were majorly analysed, based on their structure, functional groups and performance. In the characterization of the chemical structure of the lignins, solid samples in powder state were measured via FTIR, by using attenuated total reflection infrared spectroscopy (ATR-IR). In addition to that, the different lignin samples were subjected to High Performance Size Exclusion Chromatography (HPSEC) to evaluate their average molecular weight (Mw) and polydispersity index (PDI). For the study of the main lignin functional groups, namely hydroxyl groups, ^{31}P-NMR analysis was employed. The thermal properties of lignins were measured by DSC and TGA.

3. RESULTS AND DISCUSSION

The Results and Discussion section provides an in-depth analysis of the raw materials, delignification processes, lignin, and cellulose nanofibers. The characterization of raw materials reveals key components such as cellulose, lignin, hemicellulose, and extractives, highlighting their suitability for further processing. Variations in the chemical composition across these materials, along with the mass balance, are discussed to understand their impact on subsequent treatments. The delignification processes are compared in terms of their efficiency in removing lignin while preserving cellulose. The thermal and structural properties of the delignified pulps are examined, emphasizing differences in degradation temperatures, residue formation, and the effectiveness of each method in altering the material's composition. Lignin analysis focuses on its removal during delignification, with a detailed evaluation of its thermal stability and residual presence in the pulps. The effect of lignin on the thermal properties of the materials is discussed, illustrating how different delignification methods impact its retention and removal. Additionally, the quality of lignin is examined in relation to its impact on the overall material properties. Finally, the production of nanofibers from the delignified pulps is explored. The nanofibers' morphology, size, and structural

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characteristics are analysed using AFM and TGA. The impact of surface functionalization strategies on the nanofiber's hydrophobicity, thermal stability, and compatibility with polymer matrices is also addressed, offering insights into their potential for composite applications.

3.1. RAW MATERIAL CHARACTERIZATION

In this section, the results obtained from the characterization of the raw materials are discussed, including the mass balance and structural analysis. The structural analysis is represented through FTIR and TGA spectra, providing valuable insights into the composition and thermal behaviour of the materials.

3.1.1. Raw material mass balance

Figure 3 presents the composition of each raw material category (PB, FB, MW, and MRM). Cellulose content is relatively consistent across materials, with a slight decrease from PB to MW. Lignin content follows a similar trend, with PB having the highest and FB having the lowest share. Hemicellulose levels show less variation, peaking in MW and decreasing in PB. Inorganic content is comparable in PB and FB, but it drops significantly in MW. Notably, extractives vary widely: FB contains more than three times the extractives of PB, with a significant increase in its share. MRM, being a mix of PB, FB, and MW, reflects the combined composition of these materials, showing intermediate values for cellulose, lignin, and extractives.

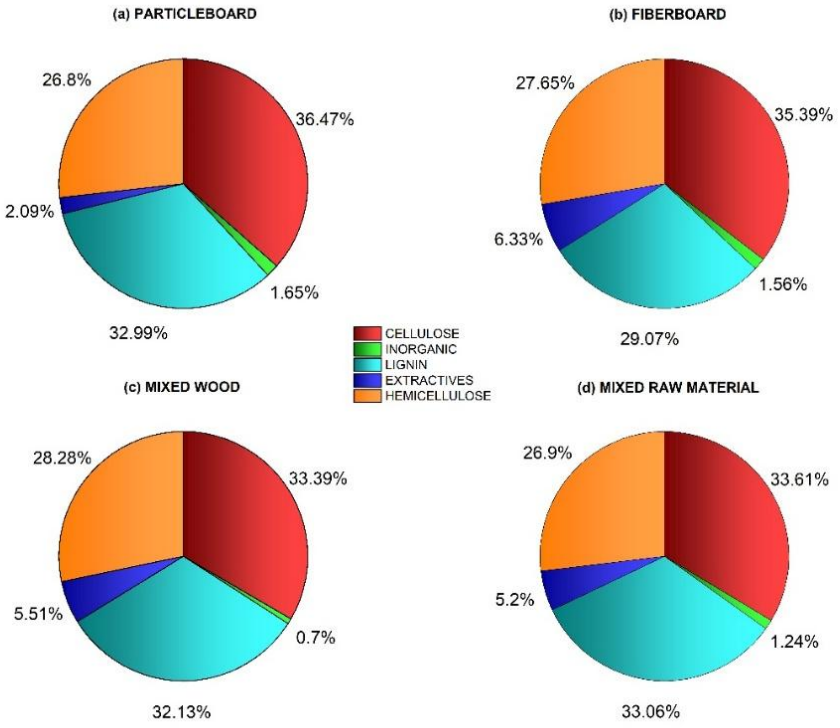

Figure 3. Composition of raw material and fractions.

The observed variations in composition across raw materials can be attributed to differences in wood type, processing methods regarding synthetic wood (PB and FB), and raw material purity. In this case, the MW category consists mainly of softwoods, which naturally have higher lignin and extractive contents (Rowell, 2005; Skaar, 1988).

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3.1.2. Structural Analysis

Figure 4(a) presents the ATR-FTIR spectra of PB, FB, MW, and MRM. The ATR-FTIR spectra highlights a few chemical differences across raw materials.

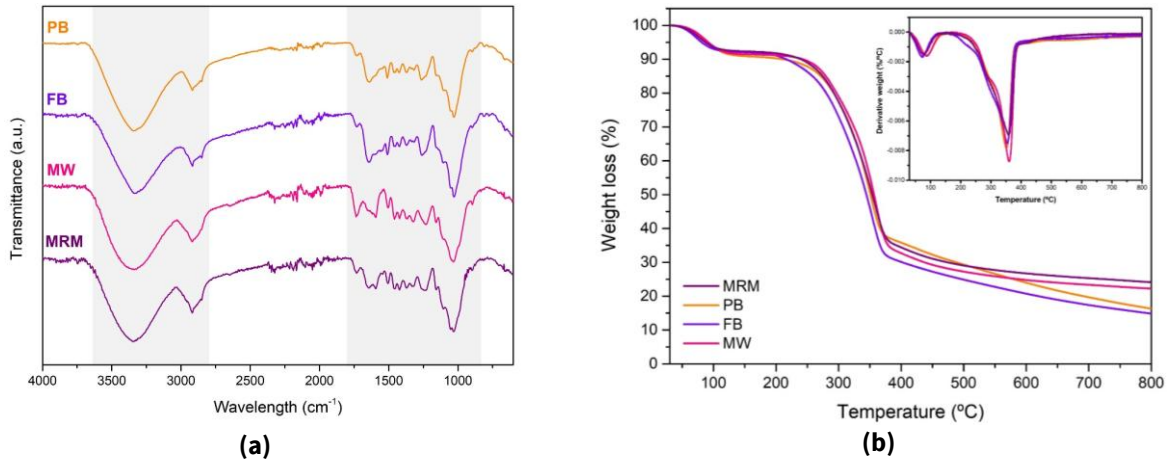

Figure 4. Structural analysis of raw materials (a) FTIR and (b) TGA.

In **Figure 4(b)**, the curves derived from the thermogravimetric analysis and derivative thermogravimetry of the raw materials (PB, FB, MW, and MRM) are presented. All the materials showed rapid degradation between 200°C and 375°C, followed by slower degradation above 375°C. Due to the minimal differences in the characteristics of the various raw materials and the heterogeneous nature of waste wood disposal, MRM was selected for this study. It represents a mixture of different types of waste wood (PB, FB, and MW), with a high share of PB as it has moderate properties and is often the most abundant component in waste wood.

3.2. PULPS AND PULPING PROCESS ANALYSIS

3.2.1. Mass balance

Alkaline delignification, represented by SP, was particularly effective in removing lipid-based extractives (lipophilic compounds), including waxes and resins, which are often more difficult to remove in milder or solvent-based delignification processes like OP and AP. However, the high alkaline conditions in SP likely contribute to the lowest yields of both cellulose and lignin. In addition to this, these harsh conditions have a direct influence over the composition of the lignins extracted, as it will be discussed in section 2.4.1. The strong sodium hydroxide not only removes extractives but also degrades cellulose and hemicellulose, leading to lower yields of these components. The increase in inorganic content in SP is primarily due to the presence of sodium hydroxide (NaOH), which contributes sodium-based compounds to the pulp. Additionally, alkali reactions with wood components and inorganic salts remain in the pulp after the soda pulping process, contributing to the higher inorganic content in SP compared to the raw material. Due to the reduced yields from SP, it was excluded from consideration in this study's delignification process, as its yields would be significantly inflated in a scale-up scenario. AP, followed by OP, indicated highly efficient delignification processes that preserve cellulose while removing a significant portion of lignin.

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3.2.2. Structural Analysis

Figure 5(a) presents the ATR-FTIR spectra of MRM and delignified pulps (AP, SP, and OP).

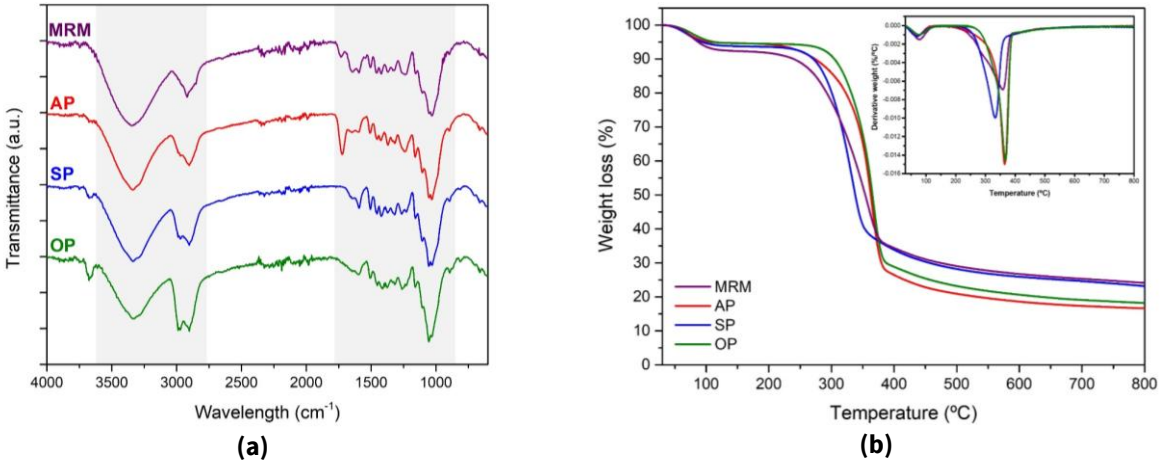

Figure 5. Structural analysis of delignified pulps compared to MRM (a) FTIR and (b) TGA.

In the delignified pulps, the intensity of peaks associated with lignin is reduced, particularly at 1600 cm^{-1} and 1640 cm^{-1}, with the greatest decrease in AP. The 1725 cm^{-1} peak, which corresponds to hemicellulose, disappears in most of the delignified pulps, except in AP, where it remains. The higher intensity of the 1725 cm^{-1} peak in AP compared to MRM suggests ester formation. Watkins et al. noticed that during the pulping process using formic acid, esterification of the phenol and alcohol of the propane chain occurred (Watkins et al., 2015).

In **Figure 5(b)**, the TGA and DTG curves for the delignified pulps (AP, SP, OP) and MRM are shown. The analysis of these curves reveals key differences in the thermal stability and degradation behaviour of the materials. In conclusion, AP and OP are the most efficient delignification processes, as they preserve cellulose while removing a significant portion of lignin and extractives, resulting in improved thermal stability and lower residues. SP, while effective in removing lipid-based extractives, is less efficient in preserving cellulose, resulting in lower thermal stability and higher inorganic content, making it less suitable for scaling up due to its lower yields and higher residue content.

3.3. PULP CHARACTERIZATION

For further characterization of the delignified pulps, structural analysis of the holocellulose and αcellulose of delignified pulps were analysed. In the FTIR spectra shown in **Figure 6**, several noticeable variations occur when comparing the delignified pulps (AP, SP, and OP) with their corresponding holocellulose (Holo. AP, Holo. SP, Holo. OP) and α-cellulose (αcell. AP, αcell. SP, αcell. OP) fractions. Key peaks that became more intense in the holocellulose and α-cellulose spectra compared to the delignified pulps are at 2990 cm^{-1}, 2900 cm^{-1}, 900 cm^{-1}, and 1400 cm^{-1}, which are associated with the C-H stretching and C-O stretching in cellulose and hemicellulose. These peaks reflect the cellulose content being more prominent in the holocellulose and α-cellulose fractions after the delignification processes. The 3680 cm^{-1} peak, which corresponds to O-H stretching, appeared in both holocellulose and α-cellulose spectra of SP and AP, and was further intensified in OP, indicating the presence of hydroxyl groups. Meanwhile, peaks around 1500 and 1600 cm^{-1}, associated with lignin (C=C stretching), reduced in intensity in holocellulose and α-cellulose spectra

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compared to the delignified pulps. In the case of AP, the 1720 cm^{-1} peak, indicating ester linkages, was reduced in holocellulose and α-cellulose spectra.

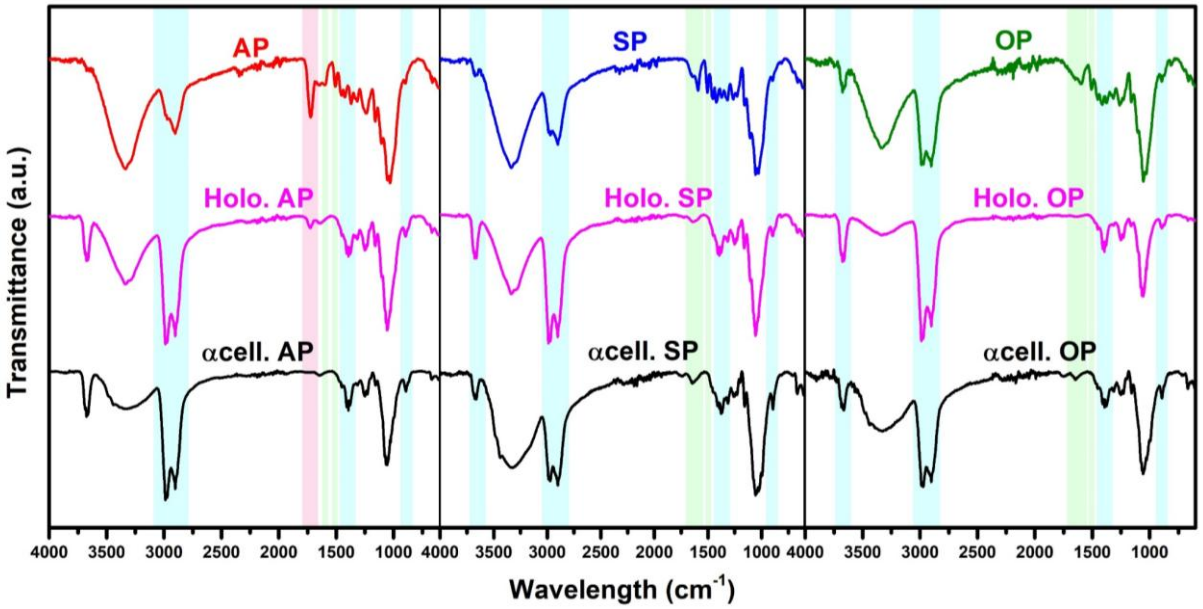

Figure 6. Pulps structural characterization (FTIR).

The FTIR results indicate that a significant amount of lignin was effectively removed. This is evident from the reduced intensity or disappearance of peaks associated with lignin. The increase in intensity for peaks associated with cellulose in the holocellulose and α-cellulose fractions compared to the delignified pulps suggests that the cellulose content was preserved or enhanced through bleaching. Additionally, the reduction 1720 cm^{-1} peak, in AP´s holocellulose and α-cellulose indicate disappearance of ester linkages after to bleaching.

Overall, all the delignified pulps exhibit better thermal performance than their corresponding holocelluloses and α-celluloses, with the exception of AP holocellulose, which has higher thermal stability than its corresponding delignified pulp.

3.4. CELLULOSE FRACTION

Lignocellulosic nanofibers were successfully produced *via* mechanical defibrillation of pulps obtained from three distinct delignification processes: acetoformosolv, soda, and organosolv. AFM was employed to characterize the topographical features of the nanofibers after homogenization under high shear forces. The AFM images (**Figure 7**) clearly demonstrate that all pulps were completely isolated to a nanoscale level. However, a comparative analysis of the AFM micrographs revealed notable differences in nanofibers morphology depending on the pulping method.

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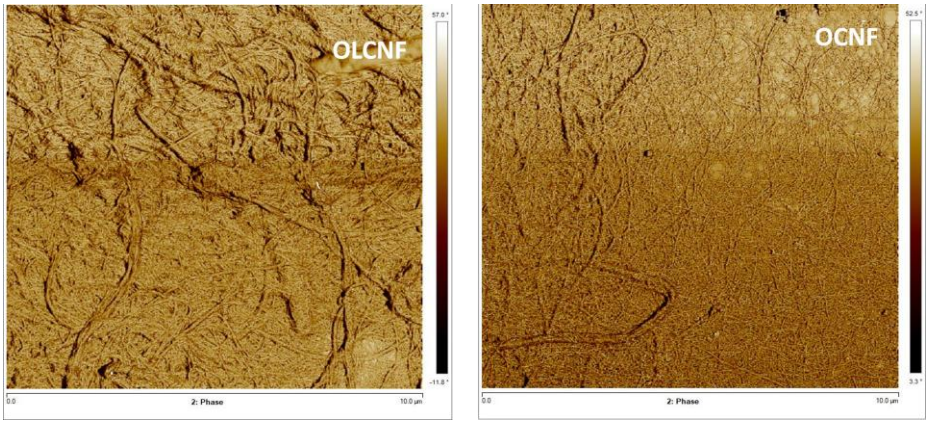

Figure 7. AFM image of nanofibers.

3.5. BLEACHING

The bleaching of organosolv pulp was carried out to assess whether the removal of residual lignin could facilitate mechanical defibrillation and improve nanofiber characteristics. The resulting nanofibers reveal that both unbleached (OLCNF) and bleached (OCNF) pulps were successfully defibrillated to the nanoscale, with average diameters of approximately 35 nm and 22 nm, respectively. While this suggests slightly finer fibrillation for the bleached sample, the overall size distribution remained comparable. The nanofiber lengths in both cases were estimated to be in the micrometre range.

To further assess the structural organization of the nanofibers, XRD analysis was conducted. Crystallinity index (CI) values, calculated from the XRD data using the Segal method (**Equation 1**), were 52.6% for OLCNF and 66.4% for OCNF. The significant increase in CI for the bleached nanofibers is attributed to the removal of amorphous components such as lignin and hemicellulose during the bleaching process, which enhances the relative proportion of crystalline cellulose domains.

$$\%\ Cristallinity\ = \left[\frac{\sum A_{Cr}}{A_T}\right] \times 100 \qquad (1)$$

3.6. CELLULOSE SURFACE FUNCTIONALIZATION

Following the comparative evaluation of bleached and unbleached organosolv nanofibers, OLCNF were selected for further use due to their balanced nanostructure, higher thermal stability, and reduced environmental impact. Their retained lignin content did not significantly hinder nanofibrillation, while offering advantages in terms of energy efficiency and sustainability. In view of their promising properties, OLCNF were chosen as the reinforcing phase for subsequent composite fabrication.

However, to ensure optimal dispersion and interfacial compatibility within the polylactic acid (PLA) matrix, surface functionalization of OLCNF was deemed necessary. The hydrophilic nature of cellulose, combined with the partial presence of lignin, typically results in poor affinity with the hydrophobic PLA, leading to unhomogenous matrix. Thus, modifying the nanofiber surface could potenailly enhance compatibility with the matrix and unlock the full reinforcing potential of the

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nanofibers. Taking advantage of the reactive hydroxyl groups available on the OLCNF surface, two distinct chemical functionalization strategies were applied:

- **Esterification** with carboxylic acid, introducing aliphatic chains that increase hydrophobicity, and
- **Silanization** using silane groups which adds amine-functional silane groups capable of promoting physical and potential chemical interactions with the PLA matrix.

3.6.1. Cellulose modification

Esterification of OLCNF was carried out using carboxylic acid as a reagent, targeting the hydroxyl functionalities present on the nanofiber surface. This reaction aims to graft short aliphatic chains onto the cellulose backbone, thereby reducing surface polarity and enhancing the hydrophobicity of the nanofibers. The success of the esterification reaction was confirmed by FTIR spectroscopy and ^{13}C NMR.

In addition to esterification, a second surface modification strategy was explored to further tailor the interfacial properties of OLCNF. This method introduces organosilane moieties onto the nanofiber surface, enabling covalent bonding between the hydroxyl groups of cellulose and the reactive silane functions. The successful grafting of silane molecules onto the surface of OLCNF was confirmed by FTIR analysis.

3.7. LIGNIN FRACTION CHARACTERIZATION

3.7.1. Characterization of the pristine lignins

The lignins obtained from the different pulping methods, without any chemical modification, namely, acetoformosolv, soda and organosolv, were analysed based on several properties.

• *Chemical composition*

The compositional analysis of the different pristine lignin was performed to determine the influence of the extraction process and their purity. Significant differences were found between the lignins extracted. Generally, the purity of the lignins is measured by the percentage of acid insoluble lignin or klason lignin. Taking this point into consideration, it was confirmed that organosolv lignin was the purest, whereas soda lignin (SL) displayed the lowest purity. The higher purity of the organosolv lignin was in accordance with other works (Erdocia et al., 2014b; Morales et al., 2020b).

• *Structure and functional groups*

The FTIR analysis was performed to evaluate the structure of the lignins and the major differences between them, owing to the extraction method implemented. In general, all the lignins displayed the typical signals along the FTIR spectra. Nevertheless, relevant differences could be detected, especially in the region of the fingerprint (1800-800 cm^{-1}). The mentioned differences were certainly a result from the different pulping method, as these are reported to influence the lignin structure (Sapouna et al., 2023).

The molecular weight of the different lignins structure was determined by means of Size Exclusion Chromatography (SEC), since it is an important parameter for the use of lignin as an additive in the

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synthesis of composites and in further chemical reactions. The results showed that all lignin extracted exhibited low molecular weights way down 5000 $g.mol^{-1}$, which is very convenient for their later use as additive in the manufacturing of composites or in a chemical synthesis. In fact, the lower the lignin size is, the higher is their solubility and dispersibility, which makes easier their processing and incorporation into materials (Li et al., 2022).

3.7.2. Modified lignin characterization

The lignin showing the most convenient properties and performance, namely, organosolv lignin, as confirmed in the previous section, was subjected to a chemical modification reaction *via* esterification. In this section, the influence of the mentioned chemical reaction over the pristine lignin structure and properties is presented.

• *Structural analysis*

The FTIR analysis was done to assess the main structural changes occurring after the chemical modification of the lignin *via* esterification. The spectra showed several changes regarding the structure and functional group confirming the modification of the lignin with the C6 fatty acid.

To complement and confirm the information extracted from the previous analysis, 31P-NMR analysis was employed as an indicator of the content of hydroxyl groups before and after the chemical modification of the lignin. The results obtained from the phosphorus nuclear magnetic resonance analysis (^{31}P-NMR) are consistent with those obtained from infrared spectroscopy (FTIR) analysis. It can be observed that both lignins exhibit a significant reduction in hydroxyl groups following the reaction with the short-chain fatty acid. This reduction was already qualitatively observed in the FTIR analysis and is now quantitatively confirmed through this analysis.

The Size Exclusion Chromatography analysis (SEC) was carried out to determine the influence of the esterification process on the molecular weight of the lignin. From the results, it was clear that the process of esterification influences the structure of the pristine lignin. In fact, a significant increment in the average molecular weight and the polydispersity index were seen. This is attributed to the introduction of ester moieties with C6 side chain, which increased both the size of the polymer and its heterogeneity. These findings were coherent with other similar works from the literature (Gordobil et al., 2017).

4. CONCLUSIONS

The W2W project, aligned with the EU's sustainability agenda, focuses on the valorisation of recycled wood derived specifically from the Construction and Demolition (C&D) sector, which represents a largely untapped yet abundant source of lignocellulosic biomass. This initiative plays a key role in transitioning to a circular economy, where resources are continually reused and regenerated, reducing dependence on virgin materials. By repurposing waste wood, W2W helps reduce environmental harm caused by deforestation, excessive waste, and rising carbon emissions, offering a sustainable alternative to the traditional "take-make-dispose" system of wood consumption. Therefore, Task 7.1 focuses on the valorisation of recycled wood through the production of nanofibers and lignin for development of PLA-based composites.

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Raw material characterization of Particleboard (PB), Fibreboard (FB), Mixed Softwoods (MW), and MRM revealed slight variations in chemical composition and thermal behaviour, with MW exhibiting the highest thermal stability. Mixed raw materials, representing a balanced mixture of PB, FB, and MW, was selected as the input for fractionation. Three delignification methods were assessed. Acetoformosolv AP and Organo pulp (OP) demonstrated the highest performance in terms of cellulose and lignin yields, effective extractive removal, and improved thermal stability. In contrast, Soda Pulp (SP) resulted in lower yields and thermal performance due to cellulose degradation and elevated inorganic content, making it unsuitable for scale-up. Further characterization of the delignified pulps and their corresponding holocellulose and α-cellulose fractions confirmed efficient lignin removal and cellulose preservation, particularly for AP and OP, as evidenced by FTIR and TGA results. XRD analysis showed increased crystallinity in bleached fractions due to hemicellulose removal, with all samples displaying characteristic cellulose I peaks. A distinct signal in SP confirmed the influence of the NaOH-based treatment.

Lignocellulosic nanofibers obtained via the unbleached organosolv route (OLCNF) exhibited optimal dimensions and moderate crystallinity (CI = 52.6%), enabling effective dispersion without requiring intensive chemical purification. Their thermal stability high char yield reflected enhanced resistance to thermal degradation due to residual lignin content. Dual surface functionalization, through esterification and silanization, successfully tuned the surface polarity, potentially ensuring improved compatibility with the PLA matrix. These physicochemical properties confirmed that omitting the bleaching step, while applying targeted surface modifications, yielded high performance nanofibers suitable for composite formulation.

In parallel, pristine lignins extracted from the same delignification routes were characterized in terms of chemical composition, structural features, molecular weight, hydroxyl content, and thermal behaviour. OP-derived lignin stood out with the highest purity, lowest molecular weight, greatest hydroxyl group content, and best thermal resistance, making it the most suitable candidate for further modification. Upon esterification with fatty acids, OL exhibited reduced hydroxyl functionality, increased molecular weight and polydispersity, and enhanced hydrophobicity, as confirmed by FTIR, ^{31}P-NMR, SEC, and solubility tests. Although esterification reduced thermal resistance slightly, it also improved processability, evidenced by a lower glass transition temperature and reduced moisture sensitivity. Consequently, both OLCNF and OLF were selected as optimized cellulose and lignin components for reinforcing PLA-based biocomposites. These findings complete the core material preparation and functionalization phase of Task7.1, setting the stage for their incorporation, performance testing, and optimization within the final composite system in subsequent tasks of WP7.

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