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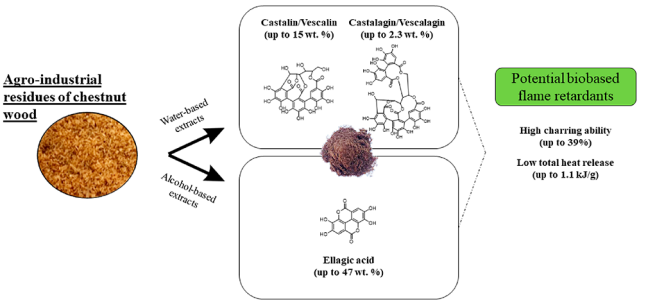
ABSTRACT: In view of their use as source material for new biobased flame retardants, chestnut wood extracts were prepared using different solvent systems and compared to an industrial extract. The prepared extracts were mainly composed of hydrolyzed products of ellagitannins (castalin, vescalin, and ellagic acid) along with saccharides. The proportions of components strongly depended on the solvent system used for the extraction. Water-based solvents promoted the recovery of ellagitannins (up to 15 wt % of dry raw matter), while the alcohol-based solvents extracted more selectively ellagic acid (up to 47 wt % of dry raw matter). The phenolic composition of the industrial chestnut wood extract completely differed from that of the lab-scale extracts. The industrial extract was mainly composed of gallic acid and nonhydrolyzed forms of ellagitannins (castalagin and vescalagin). Thermal and fire tests performed on chestnut wood extracts showed high char contents and low total heat release, varying from 33.2% to 38.8% and from 1.1 kJ/g to 6.9 kJ/g, respectively. The values mainly depended on the saccharides, ellagitannins, and ellagic acid contents of the chestnut wood extracts. These results highlighted the promising potential of chestnut wood extracts as biosourced FRs.



KEYWORDS: *Chestnut wood, Saccharides, Phenolic compounds, Biobased flame retardant*

INTRODUCTION

During the last ten years, the development of flame retardants (FRs) from renewable resources has been of growing interest.[1−4] The research community intends to find alternative to conventional fossil-sourced additives to limit the impact on the environment and human health. The research efforts were especially focused on the development of eco-friendly FRs from wood biomass due to the abundance of this resource and the facility to get products from the wood sectors.[5−12] The major wood constituents as well as other classes of biobased macromolecules such as proteins and oils were already used for the elaboration of eco-friendly FR agents.[1,2] Among wood components, cellulose and lignin were notably reported to promote the thermal resistance of polymeric materials.[13−22] The FR properties of biosourced compounds are usually associated with their elemental composition and structure that provide them the ability to promote thermally stable charred residues when exposed to fire. During the combustion, charring FR systems act by creating an insulating layer at the surface of the burning material that leads to the improvement of its fire behavior by reducing both thermal and oxygen diffusion as well as the volatilization of combustible products.

For FR application, these biobased components can be directly used. However, bioresources are often modified by introducing functional groups containing heteroatoms (most commonly phosphorus and/or nitrogen atoms) to emphasize the above-mentioned modes of action. Zhang et al.[16] showed the efficiency of lignin and its nitrogen derivatives as FR agents for the poly(lactic acid) (PLA) matrix. Untreated lignin induced a reduction of total heat release (THR) by 42% (from 71 to 41 MJ/m^2) compared to the neat PLA, while urea-modified lignin combined with ammonium polyphosphate (APP) led to the decrease of the THR value by 66% (to 24 MJ/m^2). The potential of tannic acid (i.e., gallotannins, which are another class of phenolic macromolecules) as a biosourced FR additive has been also investigated for textile, thermoplastic, and thermosetting materials.[23−25] Kim et al.[25] used tannic acid as a hardener in the epoxy thermosetting formulation to improve its flammability properties. The natural phenolic compound allowed increasing a limiting oxygen index (LOI) value by

46%, compared to the control sample. Few studies have been undertaken to date to study the thermal stability of wood extractives and their potential as FRs. In fact, most of the work carried out so far in relation to extractives aims to assess their impact on the thermal stability of wood or biomass based on thermogravimetry or pyrolysis, before and after extraction, sometimes using different solvents.[26−29] Indeed, the composition of the extractive fraction depends on both the solvent used for extraction and on the raw material. Consequently, these studies usually also include comparison between wood type (softwood vs hardwood) or wood species. The extractives constitute a heterogeneous class of numerous components that can be extracted from wood by neutral, polar, or nonpolar solvents.[30] On one side, extracts recovered with hot water (HW) usually contain inorganic matter along with polyols, simple sugars, low molecular weight polysaccharides, arabinogalactans, starch, tannins, and gums. HW extraction was proved to cause a significant decrease in the char yield of wood species and influence the thermal stability of wood.[29,31] Indeed, these components (HW extractives) are reported to promote the decomposition of natural polymers, resulting in higher char yield and lower thermal stability in the original wood compared to the HW extracted wood. On the other side, lipophilic extractives usually recovered with organic solvents composed of sterols, terpenoids, fatty acids, resin acids, and waxes are reported to play a role in influencing the ignitability of biomass because of their volatility.[32] Thus, the large availability of wood extractives makes them an interesting resource for developing applications. It is therefore crucial to carry out research to characterize the thermal properties of this material and their behavior in relation to fire in order to conceive applications as FR agents.

Sweet chestnut (*Castanea sativa Mill.*) belongs to the Fagaceae family, and it is one of the most spread chestnut species. The extractives can be recovered by green physical processes, including supercritical fluid extraction and microwave assisted extraction.[33] However, the classical solvent extraction allows a more comprehensive investigation since the number of solvents or combinations of solvents afford a greater range of polarity and selectivity compared to physical processes, which generally operate in water or conversely in apolar conditions (supercritical fluid extraction). The extractive recovery from chestnut wood by solvent extractions usually accounts for up to 16 wt % of dry raw material.[34] The chemical composition of the extracts is complex and mainly depends on the extraction conditions, including particle size, solid to liquid ratio, solvent, temperature, and duration.[33,35,36] The main constituents of chestnut extracts are both saccharides and polyphenols.[37−39] The polyphenols are hydrolyzable tannins and most notably ellagitannins such as castalagin, vescalagin, castalin, and vescalin.[40−42] Ellagic acid may also be present in high amounts.[40,41] All these molecules seem promising with regard to flame applications due to their complex aromatic structure that may promote charring, a strategy commonly used in fire retardancy of polymers.

This study aimed at identifying the relationships between the chemical composition of chestnut wood extracts and their thermal properties. Chestnut sawdust was extracted using various solvent systems in order to produce the extracts with different chemical compositions. The carbohydrate content of the prepared extracts was estimated by the anthrone method, while the identification and quantification of phenolic compounds were performed by chromatography coupled to mass spectrometry. The thermal and flammability properties of the chestnut wood extracts were evaluated by thermogravimetric analysis (TGA) and pyrolysis combustion flow calorimetry (PCFC), respectively. The results were interpreted with respect to the chemical compositions of the prepared extracts and compared to those of the industrial extract. The thermal properties of the chestnut wood residues recovered after extraction were also studied to check the consistency of the results.

EXPERIMENTAL SECTION

Materials. *Plant Material.* Fresh sawdust of chestnut was obtained on March 3, 2017 from Scierie de Jalcreste (Saint André de Lancize, France). Sawdust was oven-dried at 40 °C for 48 h and ground by a cutting mill (RETSCH SM 300) with a grid of 0.25 mm. The mean particle size measured by laser granulometry corresponded to 324 μm. The milled samples were then stored in the dark under vacuum at the ambient temperature to prevent oxidation of the phenolic compounds.

Industrial Chestnut Extract. A sample of an industrial chestnut wood (*Castanea sativa Mill.*) extract was kindly supplied as a reference.

Chemicals. Gallic acid (97.5%) was purchased from Sigma-Aldrich. Ellagic acid (97.0%) was supplied by Alfa Aesar. Vescalin (≥96.0%), castalin (≥99.0%), vescalagin (≥98.0%), and castalagin (≥96.7%) were kindly provided by Pr. Stéphane Quideau (Institute of Molecular Sciences UMR 5255, University of Bordeaux, France). All the molecules mentioned above were used as standards for the calibration. L-(+)-Arabinose (≥99%), D-(+)-glucose (≥99.5%), D-(+)-mannose (≥99%), L-rhamnose (≥99%) and D-(+)-xylose (≥99%) were purchased from Sigma-Aldrich. Sulfuric acid (95−97%) was provided from Merck. Anthrone (9-[10-H]-anthracenone) was purchased from Fluka. Folin-Ciocalteu reagent (2 N) was purchased from Merck. HPLC grade solvents (acetonitrile, ethanol, and acetone) and formic acid (≥95.0%) were provided by Sigma-Aldrich. HPLC grade methanol was purchased from VWR. Water was prepared from distilled water using a Milli-Q system (Merck-Millipore).

Extraction Conditions. Chestnut wood extractions were performed using a Carrousel 6 Plus Reaction Station (Radleys). About 500 mg of precisely weighted of chestnut sawdust was suspended in 10 mL of solvent. The sample was stirred at 60 °C for 90 min. A brown dark supernatant was collected by filtration under vacuum. The filtrate was evaporated to dryness using a rotary evaporator. The phenolic composition of extracts was analyzed by samples injection in the UPLC-DAD-ESI/MS system in conditions described below. The extraction yield was calculated for each sample. The wood residue obtained after extraction was also collected and then oven-dried at 40 °C for 24 h. All extractions were done in triplicate.

In order to evaluate the influence of solvent on the selectivity of the extracted components, pure solvents as well as mixtures of solvents were employed. Table 1 gathers the extraction conditions used and the corresponding sample labels for both the extracts and the wood residues recovered after extractions.

Methods for Extract Characterization. *Total Carbohydrate Content.* Different methods can be employed to investigate the carbohydrate content of plant extract.[43,44] In this study, the total

Table 1. Composition of Solvents Used for Extractions

solvents	volume proportions (v/v)	extracts	residues
methanol	100	M-E	M-R
ethanol	100	E-E	E-R
water	100	W-E	W-R
methanol/ethanol	50/50	ME-E	ME-R
ethanol/water	80/20	EW-E	EW-R
acetone/water	70/30	AW-E	AW-R

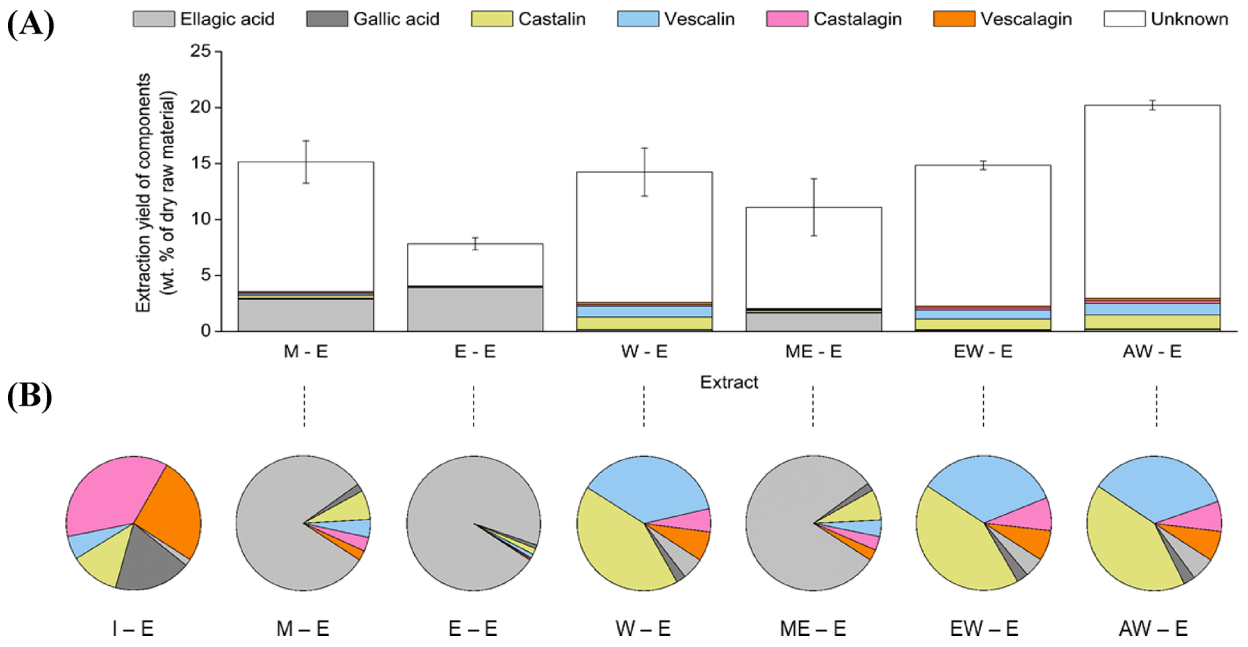


Figure 1. (A) Histograms are extraction yields (wt %) of extractives from ground chestnut sawdust, colored parts of which correspond to extraction yields of phenolic compounds. (B) Distribution of the six phenolic compounds (ellagic acid, gallic acid, castalin, vescalin, castalagin, and vescalagin) in the industrial (left) and lab-scale extracts.

carbohydrate content (TCC) of chestnut wood extracts was estimated according to the anthrone method.[45] It is a reasonable, rapid, and reproducible assay for the estimation of the soluble carbohydrate content of biomass.[46,47] Briefly, the sample solution was prepared by dissolving about 4 mg of precisely weighted chestnut extract in 20 mL of water. The anthrone solution was prepared by dissolving 0.5 g of anthrone reagent in 10 mL of ethanol and 240 mL of 75 wt % aqueous solution of sulfuric acid. One mL of the prepared sample solution was introduced into a test tube with 2 mL of 75 wt % aqueous solution of sulfuric acid and 4 mL of anthrone solution. The tube was then vortexed. After having been boiled in the heating block at 100 °C for 15 min, the sample was placed in the ice bath for 5 min. The hydrolysis and conversion of monosaccharides into furfural derivatives were considered complete under these conditions. Absorbance of the sample at 578 nm was measured by a UV−vis spectrophotometer (SAFAS UV mc2). A standard graph of glucose was plotted (concentration [mg/mL] vs optical density) from a stock solution of 0.5 g/L to determine the TCC. The TCC was expressed as glucose equivalents (in milligram Glc eq per gram of dry matter). All extracts were analyzed in triplicate.

UPLC-DAD-ESI/MS Analysis. The phenolic composition of the chestnut wood extracts was examined by the UPLC-DAD-MS/ESI system. The apparatus was composed of an Acquity Ultra Performance Liquid Chromatography UPLC (Waters, Milford, MA) coupled with a Diode-Array Detector DAD and an ion trap mass spectrometer MS (Bruker Daltonics, US). The analytical column used was Acquity HSS T3 (100 mm × 2.1 mm, 1.8 μL particle size, Waters, Ireland). The binary mobile phase consisted of solvents A (H_2O/HCOOH, 99.9:0.1, v/v) and B (pure CH_3CN). The following gradient elution was applied: from 0 to 2.5 min, 99−80% A; from 2.5 to 7 min, 80−1% A; from 7 to 8 min, 1% A; from 8 to 9 min, 1−99% A. The flow rate was fixed at 0.55 mL/min. The column was held at 38 °C, and the sample tray was set at 10 °C. The injection volume was 2 μL. The DAD was set at 280 nm. The MS analyses were performed using an electrospray ionization source operating in the positive mode in the range of 115−1500 m/z. A drying gas flow of 12 L/min, a drying gas temperature of 200 °C, a nebulizer pressure of 3.03 bar, and capillarity voltages of 4500 V were used.

The samples of chestnut extracts were prepared by dissolving about 5 mg of a precisely weighted sample in 10 mL of methanol (M-E, E-E, and ME-E) or water (I-E, W-E, EW-E, and AW-E). One hundred μL of sample solution was mixed with 900 μL of methanol or water and injected directly in the UPLC system.

Stock solutions of gallic acid, ellagic acid, castalin, vescalin, castalagin, and vescalagin were prepared by dissolving the corresponding analytical standards in methanol (for ellagic acid) or water (for the other molecules) to a specific concentration. Each solution was prepared at 5 concentrations (initial concentration and diluted 4:5, 3:5, 2:5, 1:5; v/v) in order to provide a range of signals suitable for determining the relative response factor (RRF_x). The calibration measurements were done in triplicate for each molecule.

Thermogravimetric Analysis. Thermogravimetric analyses were performed using a TGA Q50W/MFC apparatus (TA Instrument). The initial weight of each tested sample was approximately 10 mg. The samples were heated from 25 to 700 °C at 10 °C/min under nitrogen flow (40 mL/min). Degradation temperatures (T_{max}) and char yields at 700 °C ($Char_{700}$) were determined for each sample. All samples were tested in triplicate.

Flammability Analysis. Flammability properties were assessed by pyrolysis combustion flow calorimetry (PCFC) using an instrument of Fire Testing Technology (FTT UK). Around 15 mg of extract sample and about 2 mg of residue sample were placed in the pyrolyzer, undergoing an increase of temperature from 100 to 750 °C at 1 °C/s under nitrogen atmosphere. Decomposition gases were then sent to a combustor, where they are heated at 900 °C under airflow (N_2/O_2 = 80/20). In these conditions, combustion was considered as complete. The heat release rate (HRR) value was determined by oxygen depletion according to Huggett's relation (1 kg of consumed oxygen corresponds to 13.1 MJ of heat released).[48] The peak of heat release rate (pHRR), the temperature of pHRR (T_{peak}), and the total heat release (THR) were measured for each sample. The effective heat of combustion (EHC) represents the released heat by mass loss. The EHC values were calculated as a ratio between THR and the mass loss measured from TGA experiments. All the samples were analyzed in duplicate.

RESULTS AND DISCUSSION

Chestnut Wood Extraction. Chestnut wood extracts of various chemical composition were obtained using protic solvent systems of different polarities. The extractions were

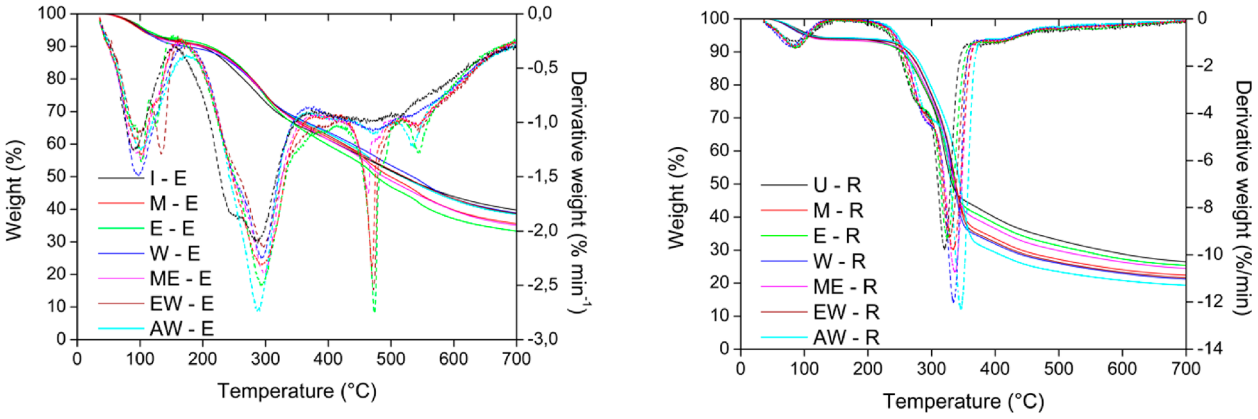


Figure 2. Thermograms of the chestnut wood extracts (left) and residues (right) at 10 °C min^{-1} under nitrogen flow as a function of solvent nature compared to the industrial extract (I-E) and the untreated chestnut wood (U-R).

performed at constant temperature (60 °C) and duration (90 min), whereas the solvent system was different for each sample.

The extractive yield obtained from chestnut wood was found to be strongly influenced by the solvent nature (Figure 1). The highest and the lowest extractive yields were obtained for AW-E and E-E, respectively. They were equal to 20.22 ± 0.42 and 7.83 ± 0.54 wt %, respectively. The extractive yields obtained with the other solvents corresponded to intermediate values that do not significantly differ from each other, except for ME-E and EW-E.

Chemical Analysis of the Chestnut Wood Extracts. *Total Carbohydrate Content of the Chestnut Wood Extracts.* The industrial extract showed the largest TCC value compared to the lab-scale extracts. The TCC value of I-E was equal to 286 ± 15 mg Glc eq/g of dry matter, while it ranged from 45 ± 14 to 141 ± 16 mg Glc eq/g of dry matter for E-E and W-E of lab-scale extracts, respectively. The difference in TCC between lab-scale and industrial extracts was mainly assigned to different extraction processes and/or wood origin. Differences between lab-scale extracts themselves come solely from the solvent nature. Indeed, saccharides usually show poor solubility in absolute methanol and ethanol, better solubility in water−alcohol mixtures, which increases with water content, and finally a large solubility in pure water.[49] Therefore, the saccharide solubility and thereby the TCC values of the lab-scale extracts increased with the polarity of the solvent system (pure or in mixture).

Phenolic Composition and Quantification. The extraction yields of the six phenolic molecules (Figure 1A) ranged from 2.05 ± 0.35 to 4.07 ± 0.34 wt % of dry raw material for ME-E and E-E, respectively. The phenolic fraction of the lab-scale extracts represents between 12.52 ± 0.27 and 48.05 ± 1.66 wt % of dry matter, depending on the solvent used for the extraction. Moreover, the distribution between the six phenolic compounds also varies according to the presence or not of water in the solvent used for extraction (Figure 1B). Indeed, the extracts obtained from alcohols mainly contain ellagic acid, whereas the extracts obtained with aqueous solvents mainly contain ellagitannins, especially, castalin and vescalin. Owing to the hydrophobic nature of the aromatic dilactone structure, ellagic acid is preferably extracted by ethanol, whereas the hydrolyzed ellagitannins, vescalin and castalin, which exhibit a sugar moiety with free hydroxyl groups liberated by hydrolysis, are more soluble in aqueous solutions.

The outstanding finding is that the main phenolics present in the lab-scale extracts correspond to the two products of ellagitannin hydrolysis. The first one is ellagic acid resulting from spontaneous lactonization of the hexahydroxydiphenic acid (HHDP) released from hydrolysis. The second one is vescalin or castalin (depending on the parent isomer vescalagin or castalagin, respectively) corresponding to the residual C-glucosidic moiety resistant to hydrolysis. The moderate temperature (i.e., 60 °C) applied in lab extractions suggests that hydrolysis occurred prior to extraction rather than in the course of lab experiments. Actually, it is well-known that hydrolysis of ellagitannins occurs through aging.[42,50,51]

The chemical composition of the industrial chestnut wood extract (I-E) shown in Figure 1A strongly differs from the composition of lab-scale extracts. Indeed, I-E is mainly composed of gallic acid and the intact (nonhydrolyzed) forms of ellagitannins−castalagin and vescalagin. This is likely explained by the different origin and age of chestnut trees. Indeed, Garcia et al.[39] reported on the influence of geographic location on the chemical composition of plants. The sawdust used as raw material in this study comes from a chestnut groove in the south of France that was little exploited since the closure of tannin factories in the 1960s. The industrial extract is produced by pressurized hot water extraction from chestnut trees slaughtered between 20 and 40 years old throughout central Europe.

Thermal Properties of the Chestnut Wood Extracts and Residues. *Thermogravimetric Analysis.* Thermal properties of biomass can be strongly influenced by its chemical composition.[52] Industrial and lab-scale chestnut wood extracts were first analyzed then treated. Chestnut wood residues were compared to untreated sawdust (U-R).

Industrial and Lab-Scale Chestnut Wood Extracts. The extracts produced in the laboratory mainly showed a similar four-step process of thermal decomposition (Figure 2). The initial step of degradation occurred between 30 and 130 °C. It was mainly associated with the elimination of moisture as well as the evaporation of solvent. The second and major step of degradation occurred in a temperature range of 150−360 °C with T_{max} values varying between 280 and 306 °C. This step can be assigned to the decomposition of saccharides. Indeed, the mono- and disaccharides were previously identified in chestnut wood extracts.[53,54] They are mainly composed of arabinose, fructose, glucose, and xylose. Arabinose, fructose, and glucose are the dominant neutral sugars of the chestnut

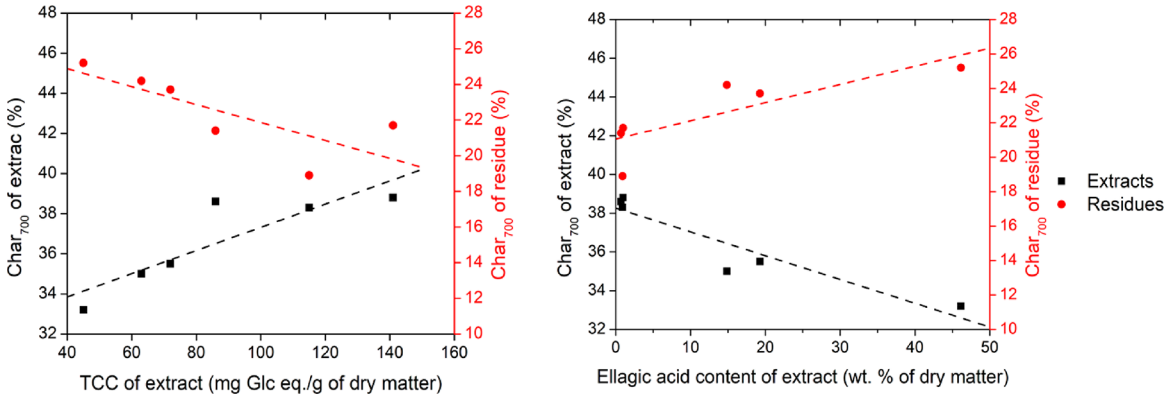


Figure 3. (A) Char yield at 700 °C of the chestnut wood extracts and residues versus total carbohydrate content (TCC) in the associated chestnut wood extracts. (B) Char yield at 700 °C of the chestnut wood extracts and residues versus ellagic acid content in the associated chestnut wood extracts. The standard deviations of triplicate assays are available in the Supporting Information.

wood extracts. According to the TGA measurements (available in the Supporting Information), these molecules decompose in the temperature range of 200−350 °C. It corresponds to the second decomposition step of the chestnut wood extracts. The third and fourth steps of degradation occurred from 430 to 500 °C and from 500 to 700 °C, respectively. They can be correlated to the thermal decomposition of ellagic acid and ellagitannins (including castalin, vescalin, castalagin, and vescalagin). According to the literature[55] and the thermogravimetric assay in the laboratory, ellagic acid displays high thermal stability. The onset of its thermal decomposition occurred at 380 °C, followed by two steps at 463 and 596 °C. These values almost correspond to the third and fourth decomposition steps of the chestnut wood extracts of the present study. The slight mismatches can be essentially due to the interactions of ellagic acid with other components of the chestnut wood extract. In addition, there is a correlation between the mass loss rate and the amounts of ellagic acid in the chestnut wood extracts. Indeed, E-E contained the highest amount of ellagic acid and showed the highest mass loss rates for the third and fourth degradation steps −2.34 and 1.08 wt %/min, respectively, whereas I-E extract was characterized by the lowest content of ellagic acid and presented the lowest mass loss rates for the same steps −1.02 and 0.78 wt %/min, respectively. The thermal properties of ellagitannins cannot be studied because of their high cost. However, it was suggested that they exhibit the same degradation profile as ellagic acid in view of their similar chemical structure. Therefore, the two last decomposition steps of the chestnut extract can be assigned to ellagic acid and ellagitannins. It is important to note that very little information is available on the thermal decomposition and pyrolysis of plant extracts.[27,56]

The industrial and lab-scale extracts displayed significant char yield at 700 °C. The $char_{700}$ of I-E was equal to 39.6 ± 0.1%, whereas the char contents of the lab-scale extracts ranged between 33 and 39%. Due to their important char yield, the chestnut wood extracts have the potential to be employed as biosourced FR component. Despite the fact that the $char_{700}$ values of the extracts were close to each other, an interesting tendency was observed. The char content was increasing with the amounts of saccharides and ellagitannins (castalin, vescalin, castalagin, and vescalagin) and was decreasing while the ellagic acid content was increasing (Figure 3). The higher the saccharide and ellagitannin contents were present in the chestnut extract, the more important char yield was observed. On the contrary, the higher the ellagic acid content was observed in the extract, the smaller char yield was noticed. Therefore, it suggests that saccharides and ellagitannins promote the charring ability of wood biomass, while the ellagic acid content weakens it.

Untreated Sawdust and Treated Chestnut Wood Residues. The mechanism of the decomposition of chestnut wood has already been investigated by the researchers.[34,52] The nonextracted sawdust and chestnut wood residues after extraction exhibited a unique three-step degradation profile (Figure 2). The first step of degradation occurred between 30 and 130 °C. It is mainly assigned to solvent and moisture evaporation. The second and major step of degradation was observed from 200 to 370 °C with a first shoulder noticed between 270 and 280 °C, and a second shoulder ranged between 320 and 344 °C. This step can be associated with the decomposition of hemicellulose and cellulose. According to the literature, the thermal decomposition of hemicellulose occurs in one main step between 220 and 320 °C with the maximum mass loss rate at around 270 °C.[57] Cellulose decomposes in a higher temperature range (310−410 °C) with the maximum mass loss rate at around 370 °C.[58] Therefore, the first shoulder (270−280 °C) can be easily assigned to hemicellulose, while the second shoulder (320−344 °C) is related to cellulose. The third and final step of degradation occurred between 370 and 450 °C and can be assigned to the thermal decomposition of lignin. It decomposes over a broad temperature range (200−500 °C) in two main steps at a very low mass loss rate: the first one from 230 to 260 °C and the second one from 275 to 450 °C.[52,57,58] The second decomposition step of lignin matches with the third decomposition step of the chestnut wood.

It was observed that the thermal stability and the char content of the chestnut wood were influenced by the extraction treatment (Figure 3). As for the thermal stability, the solvent treatment of the chestnut wood by different solvent systems induced an increase of the T_{max}. The chestnut wood residues showed T_{max} values ranging between 324 and 345 °C according to the solvent nature, while the untreated chestnut wood (U-R) exhibited T_{max} equal to 320 °C. The entire thermogravimetric curves of the chestnut wood were displaced toward higher temperatures after the extraction. Moreover, it was noticed that the T_{max} values of the studied wood residues were increasing while their saccharide and ellagitannin contents were decreasing. Indeed, it was initially considered

Table 2. Data of the PCFC Measurements (pHRR: Peak of Heat Release Rate; T_{peak}: Temperature of pHRR; THR: Total Heat Release; EHC: Effective Heat of Combustion) of the Chestnut Wood Extracts and Residues as a Function of Solvent Nature and Compared to the Industrial Extract (I-E) and the Untreated Chestnut Wood Residue (U-R)

extract name	peak HRR (W/g)	T_{peak} (°C)	THR (kJ/g)	EHC (kJ/g)	residue name	peak HRR (W/g)	T_{peak} (°C)	THR (kJ/g)	EHC (kJ/g)
I-E	8.0	260	0.9	1.5	U-R	130.2	316	9.2	12.4
M-E	25.5	275	4.2	6.4	M-R	129.6	333	10.8	14.1
E-E	37.8	256	6.9	10.4	E-R	130.6	323	9.7	13.0
W-E	6.4	290	1.1	1.8	W-R	151.3	335	12.3	15.7
ME-E	24.8	278	4.7	7.3	ME-R	140.4	337	10.9	14.4
EW-E	16.0	292	2.7	4.6	EW-R	126.1	328	10.1	12.8
AW-E	22.8	248	2.4	4.5	AW-R	150.9	349	12.1	14.9

that the untreated chestnut wood contained a constant amount of saccharides and ellagitannins. The extraction process led to remove them in various proportions depending on the solvent system used. The higher the saccharide and ellagitannin content in the extract, the less they were in the corresponding wood residue. It was then observed that the thermal stability of the wood residues increased with the amount of the saccharides and ellagitannin content in the associated extracts. Therefore, the lower the saccharide and ellagitannin content is present in the wood residue, the higher the thermal stability was observed. In addition, ellagic acid promotes the thermal stability of the chestnut wood residue. The residue exhibiting the higher ellagic acid content showed the most important thermal stability. It may be then assumed that the saccharides, ellagitannins, and ellagic acid considerably impact the thermal stability of wood biomass. Concerning the char content of the chestnut wood, it was significantly reduced by the extraction treatment. The $char_{700}$ value of the untreated chestnut wood (U-R) was equal to 26.3% and corresponded to the value reported in the literature.[34] The $char_{700}$ values of the chestnut wood residues ranged between 18 and 25% according to the saccharide, ellagitannin, and ellagic acid contents in the associated wood extracts (Figure 3). The observed tendencies for the T_{max} and the $char_{700}$ values were also reported in previous works. It was mainly associated with a decrease of the fixed C-content in the resulting char.[31,34,59] However, it has not been associated with the saccharide, ellagitannin, and ellagic acid contents of wood biomass in particular.

Pyrolysis/Combustion Flow Calorimetry of the Chestnut Wood Extracts and Residues. Thermogravimetric assay can be completed by the study of the flammability properties of the chestnut wood products using pyrolysis/combustion flow calorimetry PCFC as this technique is well adapted for the study of polymers combustion[60] and since the heat of combustion of biomass components is much higher than the pyrolysis heat.[61] In all cases, similar profiles of degradation were obtained from TGA and PCFC experiments.

Industrial and Lab-Scale Chestnut Wood Extracts. As is shown in Table 2, the I-E showed pHRR and THR values equal to 8.0 W/g and 0.9 kJ/g, respectively. Some differences in the PCFC measurements of the lab-scale extracts were marked. Their T_{peak} values ranged from 248 to 292 °C for AW-E and EW-E, respectively. The most significant variation in the pHRR was noticed between W-E and E-E — 6.4 and 37.8 W/g, respectively. The THR values of the lab-scale extracts were small and varied from 1.1 to 6.9 kJ/g for W-E and E-E, respectively. It can be associated with the important char yield of the extracts, which reduces the amount of fuel and thus the THR values. It was also observed that the THR values were decreasing with decreasing ellagic acid content and increasing saccharide and ellagitannin contents. This is consistent with the fact that saccharide and ellagitannin promote charring. The same tendency was observed for the EHC parameter. EHC reflects the energy released by the combustion with respect to the amount of pyrolysis gas. Since char residues are carbon-rich, the higher the char yield is, the lower the ratio C/O is in the pyrolysis gases. Therefore, species that promote charring are also prone to reduce EHC. It is especially interesting for the FR application where low combustion energy is targeted.

Untreated and Treated Chestnut Wood Residues. The untreated chestnut wood showed the T_{peak} and the pHRR values equal to 316 °C and 103.2 W/g, respectively. The entire HRR curves of the chestnut wood residues were displaced toward higher temperatures after the treatment. The peak of HRR appeared in the temperature range from 323 to 349 °C, and its intensity varied from 126 to 151 W/g. The THR values of the chestnut wood residues were between 9.7 and 12.3 kJ/g. The relationship between the THR and EHC measurements of the chestnut wood residues and the saccharide, ellagitannin, and ellagic acid content was the same as for the chestnut wood extracts.

CONCLUSIONS

Chestnut wood extracts were prepared using different solvent systems. The saccharide content as well as the phenolic content (ellagic acid, gallic acid, castalin, vescalin, castalagin, and vescalagin) of chestnut wood extracts was estimated. It was observed that the chemical composition of extract was strongly influenced by the nature of the solvent system. The water-containing solvent systems were more suitable for the recovery of saccharides and ellagitannins, while the alcohol-containing solvents were much more suitable for the extraction of ellagic acid. Thus, it is important to select an appropriate solvent system to obtain the extract with convenient chemical composition.

The chestnut wood extracts showed a high char content at 700 °C and low THR values. It was observed that the char content of both extracts and residues was increased with the saccharide and ellagitannin contents and decreased while the ellagic acid content was increased. However, the THR and EHC values of the extracts and residues showed the opposite tendency. The extract prepared with water showed the highest char content and the lowest THR values. The industrial extract exhibited similar thermal behavior as the extract obtained with water. Therefore, the chestnut wood water-based extract seems to have a potential as biosourced FRs because of its remarkable thermal properties and the ease of implementing at an industrial scale the corresponding extraction process. On the other hand, ellagic acid best extracted by alcohols can be a

good building block for developing materials requiring good thermal resistance, including epoxy resins.

Perspectives in the Biobased FR Field. To go further into the development of FRs from renewable resources, a fractionation to separate saccharides and phenolics in the lab-extracts is planned. Then, the saccharide fraction will be more precisely analyzed to have a good overview of the saccharide composition. The thermal properties of both the phenolics and saccharide fractions will be investigated and compared to the results reported herein to evaluate their respective contribution and/or synergy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b03000.

Size distribution of chestnut wood powder, extraction yields of chestnut wood, results of chemical characterization of chestnut wood extracts as well as thermogravimetric and PCFC characteristics of chestnut wood extracts and residues (PDF)

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Notes

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