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Assessment of Agroforestry Residues: Their Potential within the Biorefinery Context

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S *Supporting Information*

ABSTRACT: The concept of bioeconomy has been promoted worldwide in order to replace fossil-based resources and to find new strategies for waste management, by converting biomass into energy, chemicals, and value-added products, in a sustainable way. Despite the efforts that have been made in this area, there are still some unexplored raw materials globally, namely from agricultural and forestry industries. Therefore, the aim of this work was to characterize four abundant residues from the Portuguese agroforestry industry, including pruning residues (pine branches, PB) and stumps (PS), tomato waste (TW), and winery wastewater (WW), for analyzing their potential within the biorefinery context. Volatiles were analyzed by gas-chromatography, and compounds with repellent/attractant properties were found for PB and PS, while flavor-enhancers were particularly identified in agrowastes. Composition analysis revealed that both TW and WW had the potential for biogas generation (BMP ~340 and ~250 NL CH4/kg VS, respectively), whereas forestry residues (PS and PB) can be recovered for thermal energy (HHV ~20 MJ/kg) and bioethanol production (~0.3−0.4 L/kg). Among all the aqueous extracts that were obtained, PS showed both the highest antioxidant activity (IC$_{50}$ ~6 μg/mL) and total phenolic content (~400 mg GAE/g extract). All residues were demonstrated to be promising for the Portuguese biobased economy.

KEYWORDS: *Biorefinery, Agroforestry residues, Pine, Winery wastewater, Tomato, Valorization, Energy*

■ INTRODUCTION

The biorefinery concept is nowadays an essential strategy to convert biomass residues into value-added products and energy.[1] In fact, the European Union has been encouraging the use of renewable raw materials and their conversion into energy, to achieve sustainable growth in the context of the bioeconomy and circular economy strategies.[1] Among the waste materials (agricultural, industrial, zootechnical, fishery, and forestry wastes), more than 120 million tons per year correspond to crop residues, while 40 million tons per year are originated from the forestry industry, with these two sectors being responsible for 30% of the waste produced in Europe.[1,2] From a biorefinery perspective, the main use of these residues is the energetic route. There is a lack of data regarding the assessment of the potential of lignocellulosic materials,[3] such as agricultural and forestry residues, for other applications, from a more holistic approach.[4] In Portugal, a similar situation is observed,[5] and some residues have not been valorized yet. Thus, a "National plan for the promotion of biorefineries", with a strategy until 2030 was developed by the Portuguese Government to promote a sustainable use of renewable resources and to take advantage of readily available residues from residual and natural biomass sources.[6] In this context, it is important to identify and to characterize easily accessible residues, not explored until now, and to assess their potential to produce innovative value-added products.

Forestry biomass is the most relevant renewable source of bioenergy in Europe. In Portugal, the forest area corresponds to 35% of the national surface (13 million m^3 production), generating distinct wastes from this economic activity. Primary forestry residues include logging residues, stumps, and early thinning (e.g., branches), while secondary residues correspond to those from the wood processing.[1] These wastes (e.g., from wood and bark) have adequate heating value to produce thermal energy, and hemicelluloses and lignin content make this type of materials suitable for obtaining second-generation biofuels, such as biogas and bioethanol.[7] Cellulose and hemicelluloses can be used in food, textile, paper, petroleum, and mining industries,[8] among others. The worldwide industrial production of lignin is ca. 70 million tons, but only 1% is used as chemical precursors and materials manufacture, in spite of its potential for the production of aromatic substitutes, nowadays derived from petroleum.[9] Other less explored products may be obtained from pine residues, especially for food and pharmaceutical applications,
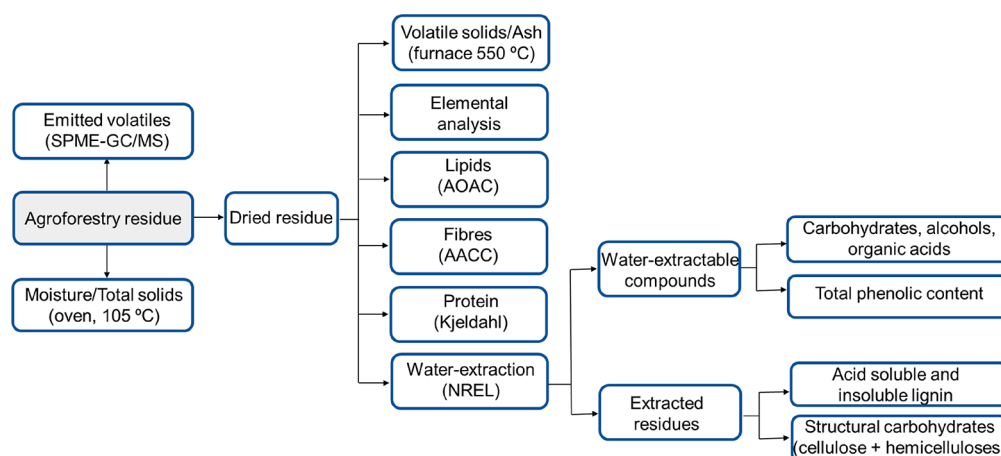
Figure 1. Diagram of the analyses performed on the four agroforestry residues for evaluating their composition.

due to their phenolic content and antioxidant activity.[10] Pine residues are also sources of important volatiles in ecosystems, with some of them being repellents or attractants, that mediate the interaction of the tree with insects and pathogens.[11]

The agricultural sector also produces a large amount of wastes, as already mentioned, with straw (wheat, barley, and rapeseed) being the most promising in the European bioeconomy approach. Agrowastes usually include materials such as stalk, leaves, peel, seed, or pulp from fruits, legumes, or cereals.[3] Nonedible parts of plants, postharvest or postprocessing food residues, are also sources of valuable compounds and energy.[12]

Portugal is one of the largest European producers of tomato (1.2 million tons by 2018),[13] and the tomato pulp industry generates about 8% of residue (d.b), which is mainly composed of seeds and peel.[14] Other residues include those from the crop growing, packaging, storage, and sale, which include plant remains, green tomato fruits, and red unmarketable fruits.[15] Such materials are inexpensive resources, rich in bioactive compounds and antioxidant ingredients.[15] The corresponding volatiles[16] may be extracted, and they have been investigated in order to promote the desirable aroma in tomatoes and to avoid the loss of their traditional organoleptic characteristics. The extraction of carotenoids, from tomato pomace,[17] has also been explored since these compounds have antioxidant properties and may provide health benefits.

Many wastes are also generated from the winery industry, mainly from Southwestern Europe (Italy, France, Greece, Portugal, and Spain), which is responsible for almost 50% of worldwide wine production.[1] In Greece, for example, ~5 MhL of wine are produced per year,[18] resulting in about 5 tons of waste per hectare of land, during cultivation and harvesting, and in 650,000 m³ of winery wastewater.[19] Portugal is the 12th wine producing country worldwide with 6.6 MhL in 2017,[20] and therefore, the amount of winery wastes generated is, at least, similar to Greece values. Residues from the winery industry may be obtained from the pruning activities and from the process of wine elaboration. These residues have lignocellulosic nature, as well as phenolics, tannins, and anthocyanins, therefore having the potential to be used in food, cosmetic, and pharmaceutical industries.[1] Wine volatiles also play an important role in understanding the influence of different growing regions and other factors on wine aroma characteristics. Wine residues may be a source of those

volatiles and may have potential as flavor-enhancing compounds.[21]

Therefore, based on biorefinery and sustainable economy concepts, the aim of this work was (i) to characterize four residues easily obtained from the Portuguese agroforestry industry: pruning residues (pine branches) and stumps, tomato waste, and winery wastewater, and (ii) to evaluate, for the first time, their potential by pointing out possible uses according to the main compounds, and considering criteria to produce energy, materials, and aromatic compounds for the flavoring industry. Therefore, this is an innovative study which includes the characterization of these four residues by using many techniques in order to explore their potential for distinct applications.

■ EXPERIMENTAL SECTION

Raw Material Sampling. The four agroforestry residues were collected and preprepared for the characterization techniques (Figures 1 and S1). Pruning residues (*Pinus pinaster* branches) were collected in Coimbra (Portugal), in September of 2017. For the extraction procedures, this raw material was milled (cross beater mill, Retsch) in order to obtain a particle size <2 mm, and stored at −18 °C.

Pine (*P. pinaster*) stump chips were kindly supplied by Central Termoelétrica de Biomassa das Terras de Santa Maria (Oliveira de Azeméis, Portugal), in January of 2017, washed, milled, and sieved, to obtain a fraction with particle size in the 0.210−0.841 mm range.

Tomato (*Solanum lycopersicum*) fruits were obtained from a local store in Coimbra (Portugal), in a semirotten state, minced mechanically, and frozen at −18 °C.

The winery wastewater was formed during the production of wine spirits in a wine distillery and corresponds to the fraction that was not distilled. A sample of 40 L was kindly provided by the wine house Quinta das Bageiras (Sangalhos, Portugal), fractionated in bottles, and frozen at −18 °C.

Henceforward, these four residues will be designated as PB (pine branches); PS (pine stumps); TW (tomato waste); and WW (winery wastewater).

Chemicals. Folin-Ciocalteu's reagent, iron sulfate II (99%, p.a.), and anhydrous copper sulfate (98%, p.a.) from PanReac; sodium carbonate from Scharlau; gallic acid (97.5−102.5%), ethanol (≥99.8%, p.a.), D(−)-fructose (>99%), sulfuric acid (95−98%, reagent grade), and 1,1-diphenyl-2-picrylhydrazyl (DPPH) from Sigma-Aldrich; *n*-hexane (≥95%, p.a.) from Carlo Erba; boric acid (>99.8%, p.a.), hydrochloric acid (37%, p.a.), and potassium sulfate (>99%, p.a.) from Chem-Lab; sodium hydroxide (99%) from Labsolve; furfural (>99%), bromocresol green and methyl red from Merck; calcium carbonate (99.0%) from Alfa Aesar; anhydrous D(+)-glucose (>99%), D(+)-mannose, and L(+)-arabinose from Riedel-de

Haën; glucuronic acid and succinic acid (99%) from Acros Organics; acetic acid (99.8%) and D(+)-galacturonic acid (99%) from Fluka; glycerol (99.5%) and L(+)-lactic acid (90%) from VWR Chemicals.

Raw Materials Composition. The residues were analyzed in terms of elemental composition and content of lipids, fibers, proteins, carbohydrates, and lignin. Extractable compounds by water and volatiles were also determined (Figure 1).

The identification and semiquantification of emitted volatiles were performed before the decomposition/fractionation methodologies, since it is important to preserve the volatiles naturally emitted by the raw materials.

The solid-phase microextraction/gas chromatography−mass spectrometry (SPME-GC/MS) method was carried out, in duplicate, using the headspace mode at 35 °C, without solvents, and a 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) coated fiber (Sigma-Aldrich) to adsorb the volatiles. PB was cut into one portion *per* sample and transferred to an empty flask to have a fixed ratio of raw material *per* volume of air (1/100, w/v). The same mass/air ratio was applied for PS. In the case of agrowastes, an aliquot was transferred to a flask, to attain a ratio of 1:10 (v/v), in relation to air volume. Adsorption time was 5 min for PB and PS. For agrowastes, 10 and 15 min were needed for WW and TW, respectively. These conditions of analysis (ratio, time, and temperature) were previously optimized to allow the adsorption of volatiles by the chromatographic fiber, while avoiding their thermal degradation. The composition of the emitted volatiles was determined by coupled GC/MS (7890A, 5975 C inert MSD with triple axis-detector, Agilent Technologies). After the adsorption step, the chromatographic fiber was immediately introduced in the injection port of the GC equipment, and the trapped compounds were desorbed at 250 °C, for 1 min. The separation was achieved on a DB5-MS fused silica capillary column (30 m × 0.25 mm i.d. × 0.25 μm, Agilent J & W Scientific), using helium as the carrier gas, at 1 mL/min. The temperature program included an isothermal hold at 50 °C (5 min), followed by a temperature ramp of 10 °C/min up to 270 °C (5 min).[22] Volatiles identification was carried out by comparing their mass spectra with the libraries NIST and Flavours and Fragrances of Natural and Synthetic Compounds. The semiquantitative analysis was based on the peak relative areas of the detected compounds.

Elemental analysis (C, H, N, and S) was performed using 2 mg (dry basis), in triplicate, and an EA-1108 CHNS-O Element Analyzer (Fisons Instruments).[23] Oxygen was calculated as 100% minus the sum of C, H, N, and S.

Lipids content of residues was evaluated, in duplicate, according to the Official Methods of Analysis of AOAC International (No. 950.54),[24] using 3 g (d.b.) of raw material in 200 mL of hexane, and a Soxhlet extraction (6 h).

Fibers quantification was performed based on the method from the American Association of Cereal Chemists (AACC),[25] in duplicate, by using 3 g (d.b.), and an acid hydrolysis (1.25% H_2SO_4, 30 min) followed by an alkaline hydrolysis (1.25% NaOH, 30 min). After filtration and washing, the material retained on the filter was oven-dried (100 °C) and weighed, and the ash content was determined to calculate the fibers amount.

The protein content was evaluated in duplicate by measuring the total nitrogen present in the residues (Kjeldahl method, System 20, P. J. Selecta S. A.).[26]

Structural carbohydrates (cellulose and hemicelluloses) and lignin contents were analyzed, in duplicate, after water extraction, on the remaining residues, which were oven-dried at 40 °C for 48 h. The analysis was based on a National Renewable Energy Laboratory (NREL) standard analytical procedure (NREL/TP-510-42618 Technical Report),[27] consisting of a hydrolysis method. Concisely, 300.0 ± 10 mg of extracted and dried samples was digested (72% H_2SO_4 solution, 30 °C, 60 min), and the resulting hydrolysates were diluted and autoclaved (121 °C, 60 min). Then, they were cooled to room temperature, followed by vacuum filtration. The acid insoluble lignin was gravimetrically determined after oven-drying at 105 °C. The acid soluble lignin determination was carried out by spectrophotometry at 205 nm (Beckman DU 650). For the structural

carbohydrates analysis, the same filtrate was neutralized with calcium carbonate to reach pH 5−6, filtered, and analyzed by high performance liquid chromatography (HPLC-RI, Knauer model K-301). The identification and quantification of carbohydrates, organic acids, alcohols, and carbohydrate degradation products were performed with a Phenomenex Rezex ROA Organic Acid H+ column (300 × 7.8 mm) kept at 40 °C. The mobile phase (0.005 N H_2SO_4 solution) was pumped at 0.6 mL/min. Mannose, xylose, and galactose coelute in this column, and the global value will be expressed as mannose equivalents. Cellulose and hemicellulose contents were calculated based on the content of carbohydrates, organic acids, alcohols, and carbohydrate degradation products presented in the extracted residues.

Water-extractable compounds were obtained, in duplicate, from the freeze-dried and not comminuted agrowastes (TW and WW), and from pine residues (PB and PS), which were milled and used *in natura*. Agrowastes became fragile after the freeze-drying process, and therefore, no milling was needed. The extraction was carried out by using water, a Soxhlet extractor, a refrigeration system kept at 0 °C, and a ratio of solid/solvent of 2−10:200 (w/v, g/mL). The reflux was carried out for 6 h,[28] and the aqueous extract quantified, for yield determination. All of the dried extracts were stored at −18 °C and protected from light, until further analysis. The water-soluble carbohydrates, organic acids, alcohols, and carbohydrate degradation products in the aqueous extracts were also evaluated by the HPLC-RI method.

Aqueous Extracts Characterization. The extracts described previously were evaluated regarding their total phenolic content and antioxidant activity.

Phenolic content was determined, in triplicate, using the colorimetric Folin and Ciocalteu method.[29] Extracts were diluted in water (2 mg/mL), the Folin−Ciocalteu's reagent and a solution of Na_2CO_3 were added, and the mixture was kept in the dark for 2 h. The absorbance was read at 765 nm on a UV/vis spectrophotometer (T60 model, PG Instruments LTD),[30] and the results were expressed as gallic acid equivalents (mg GAE/g extract).

The DPPH scavenging radical assay was carried out, in triplicate, for the evaluation of the antioxidant potential.[31] The extracts were diluted in ethanol:water (50:50) and antioxidant activities were expressed as IC_{50} (μg/mL), defined as the extract concentration that is able to scavenge 50% of the DPPH radical.

Energy Production Potential. The residues were analyzed to evaluate their potential for energy production, namely regarding the high heating values (HHV) and the amount of bioethanol and biogas that could be produced.

The combustion potential for thermal energy production was evaluated by determining the HHV of the four residues. These values were calculated using the results of the elemental analysis and the standard procedure DIN 51900.[32]

Bioethanol production potential was evaluated by the volumetric yield ($Y_{V,EtOH}$), defined as the maximum volume of ethanol that could be theoretically produced *per* kg of agroforestry biomass (L/kg_residue). It was based on an established procedure[33] and estimated as Y_{EtOH} = $0.51 \times f_{total\ sugars}/0.789$, where 0.51 is the theoretical mass conversion factor of hexoses and pentoses to ethanol (kg_EtOH/kg_sugar), $f_{total\ sugars}$ is the total sugars fraction in the dry weight agroforestry residue (structural and water-soluble carbohydrates, kg/kg_bm), and 0.789 is ethanol density at 20 °C (kg/L).

Biogas production was estimated by using experimental and theoretical methods. Some parameters were evaluated for selecting the conditions of the anaerobic digestion process: total chemical oxygen demand (COD), determined by the close reflux method according to the American Public Health Association (APHA) method;[34] total solids (TS) calculated by drying samples at 105 °C until constant weight; volatile solids (VS) and ash determined by weighing the sample before and after calcination in a muffle at 550 °C for 2 h;[35] the pH measured in a suspension at a liquid to solid ratio of 10 L/kg. Anaerobic biodegradability, BD_{anae}, was estimated as the ratio of the experimental biochemical methane potential (BMP) and the theoretical maximal production (Equation S1). The BMP
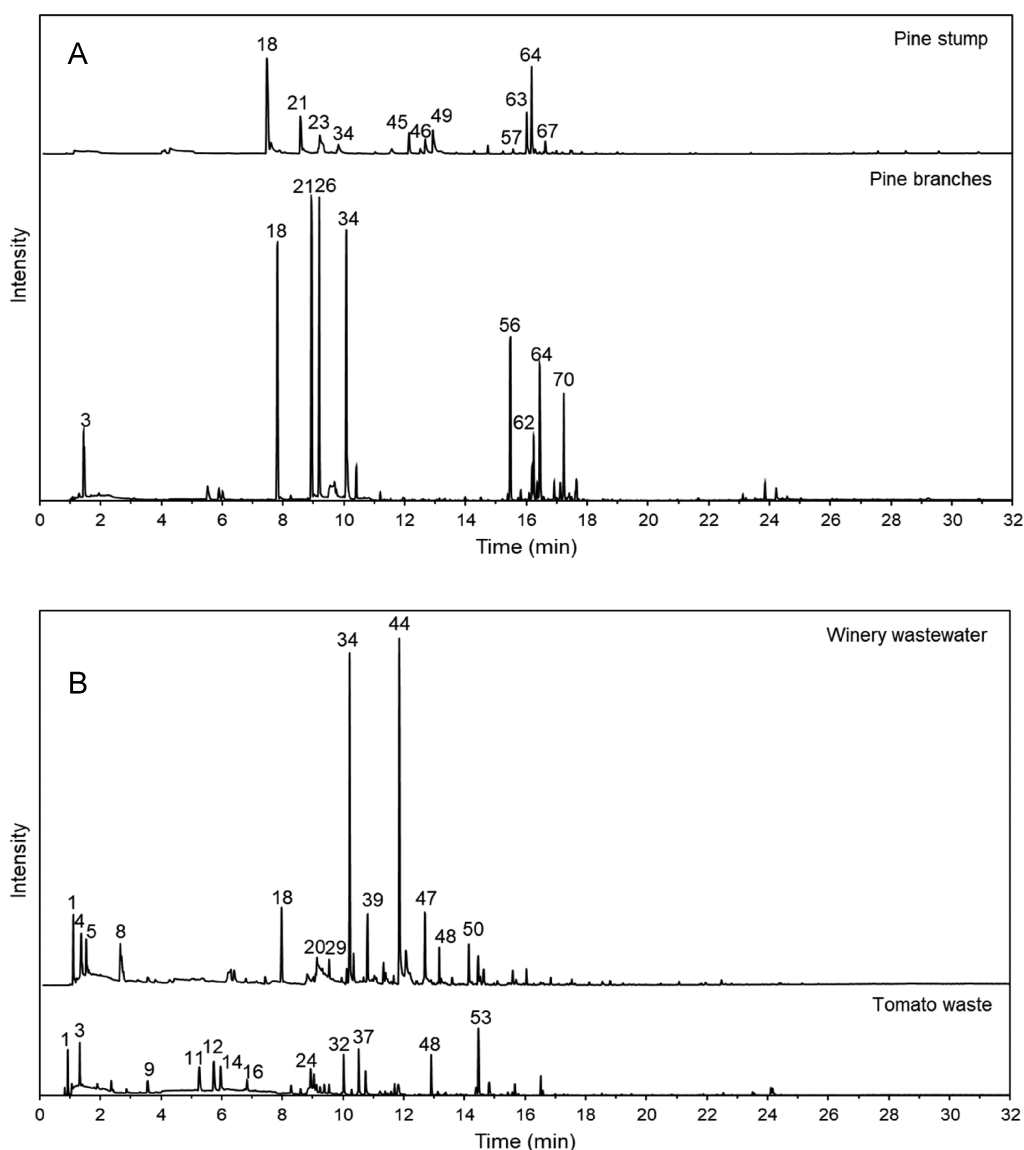
Figure 2. SPME-GC/MS profile of the volatile fraction emitted by forestry residues PB and PS (A) and agrowastes WW and TW (B). The main compounds are 1. ethanol; 3. ethyl acetate; 4. acetic acid; 5. oxaloacetic acid; 8. 3-methyl-1-butanol; 9. α-caryophyllene; 11. hex-(3Z)-enol; 12. 2-methyl-1-pentene; 14. 3-methyl-1-butanol acetate; 16. *N*-ethyl-1,3-dithioisoindoline; 18. α-pinene; 20. glycerol; 21. β-pinene; 23. sabinene; 24. 2-pentyl-furan; 26. β-myrcene; 29. ethyl hexanoate; 32. 2-isobutyl-thiazole; 34. limonene; 37. 2-octenal; 39. γ-terpinene; 44. benzeneethanol; 45. borneol; 46. 4-terpinenol; 47. 4-ethyl phenol; 48. ethyl ester octanoic acid; 49. α-terpineol; 50. 2-phenethyl acetate; 53. deca-(2E,4E)-dienal; 56. 2,4-diisocyanato-1-methylbenzene; 57. α-copaene; 62. 3,4-dihydro-2(1H)-quinazolinone; 63. longifolene; 64. β-caryophyllene; 67. α-humulene; 70. γ-amorphene.

corresponds to the methane yield at infinite anaerobic digestion (AD) time and reflects the biological decomposition of an organic substrate, and it was assessed in 5 L reactors with a working volume of 75%, at 37 °C. The biogas was quantified in a graduated gasometer sealed with a solution of NaCl 60% and pH 2. The methane was measured by washing 10 mL of biogas with NaOH 4 M to remove CO_2. Three theoretical models (MT_I to MT_III), based on chemical composition of substrates, and two multivariate regression equations (MR_I and MR_II)[36,37] were used to predict the BMP value (Table S1).

All the results presented in this work are expressed as mean ± standard deviation (SD).

■ RESULTS AND DISCUSSION

Residues Composition. Volatiles emitted by PB, PS, TW, and WW, identified and semiquantified by the SPME-GC/MS method, are included in Figure 2 and Table S2. For all the samples, the main volatiles were identified between 1 and 18 min, while a few were observed up to 28 min. Most of them are composed of 10 carbons, such as some monoterpenes (camphene, α-pinene, β-myrcene, limonene, and β-(E)-ocimene). Others contain 15 carbons, e.g. sesquiterpenes such as α-cedrene, α-cubebene, α-copaene, and longifolene, and a few volatiles are composed by 20 carbons (e.g., rimuene, abietadiene, and eicosane).

For PB, 32 compounds were identified (~94%) and special attention should be given to monoterpenes α-pinene, β-pinene, β-myrcene, and limonene and to the sesquiterpene β-caryophyllene (Figure 2). All these volatiles showed antifungal activity.[38] Therefore, PB and/or respective extracts may be applied to the control of certain fungal species. Moreover, α-pinene has been reported as an attractant for the insect vector of the pinewood nematode,[39] while limonene is a known

Table 1. Characteristics and Composition of the Four Agroforestry Residues

	Raw material	PB	PS	TW	WW
	pH	3.8 ± 0.0	4.9 ± 0.0	4.4 ± 0.0	4.2 ± 0.0
	Particle size (mm)	<2	0.2−0.8	<1	n/a
	Total solids (TS, % wt.)	40.4 ± 2.3	90.1 ± 0.2	6.0 ± 0.5	3.0 ± 0.1
	Volatile solids (VS, %wt., d.b.)	97.5 ± 0.2	97.9 ± 0.2	81.1 ± 1.2	64.9 ± 0.7
Elemental analysis	C (%wt., d.b.)	49.0 ± 0.5	46.7 ± 1.2	44.4 ± 0.2	33.9 ± 0.6
	N (%wt., d.b.)	0.9 ± 0.1	0.3 ± 0.0	3.9 ± 0.0	1.2 ± 0.0
	O (%wt., d.b.)	40.5 ± 0.6	43.2 ± 1.2	27.0 ± 0.2	25.1 ± 0.7
	H (%wt., d.b.)	7.2 ± 0.2	6.0 ± 1.6	5.7 ± 0.0	5.3 ± 0.0
	S (%wt., d.b.)	<DL	<DL	<DL	<DL
	C/N ratio	57.1 ± 3.2	136.3 ± 3.0	11.4 ± 0.1	27.5 ± 0.3
Compositional analysis	Fiber[d] (%wt., d.b.)	28.0 ± 0.8	57.0 ± 0.3	10.4 ± 0.6	0.4 ± 0.0
	Water-soluble carbohydrates (%wt., d.b.)	5.5 ± 0.2	0.2 ± 0.0	30.2 ± 2.2	5.1 ± 0.9
	Ash (%wt., d.b.)	2.5 ± 0.2	2.1 ± 0.2	18.9 ± 1.2	34.5 ± 0.7
	Lipid (%wt., d.b.)	4.1 ± 0.0	1.9 ± 0.0	2.3 ± 1.0	0.3 ± 0.1
	Protein (% nitrogen)	0.3 ± 0.0	0.1 ± 0.0	1.7 ± 0.0	1.2 ± 0.0
	Acid soluble lignin (%wt., d.b.)	1.3 ± 0.0	1.5 ± 0.0	1.8 ± 0.4	0.8 ± 0.1
	Acid insoluble lignin (%wt., d.b.)	32.1 ± 0.1	28.1 ± 0.2	18.1 ± 0.3	4.0 ± 0.7
	Cellulose (%wt., d.b.)	23.0 ± 1.9	43.4 ± 0.7	11.9 ± 1.1	4.4 ± 1.2
	Hemicelluloses (%wt., d.b.)	14.9 ± 0.0	22.6 ± 0.2	8.0 ± 1.4	1.3 ± 0.3
	Water-soluble compounds[b] (%wt., d.b.)	5.7 ± 0.2	0.2 ± 0.0	32.3 ± 1.9	48.3 ± 6.7
	Sum[c] (%wt., d.b.)	83.9 ± 2.5	99.9 ± 1.3	95.0 ± 7.3	94.8 ± 9.8

[a]n/a, not applicable; DL, detection limit (100 ppm). [b]The fraction that was detected and quantified by HPLC, including carbohydrates, organic acids, and alcohols. [c]Sum from ash to water-soluble compounds. [d]Included in the lignocellulosic fraction.

repellent and for β-caryophyllene, repellent properties were also found, particularly to the pine shoot beetle.[40,41] Other volatiles emitted by PB (Table S2) include abietadiene, the precursor of abietic acid, which is produced against pathogen attacks.[42] For PS, a total of 16 compounds were identified, corresponding to 67% of the total area (Table S2). The main volatile component of PS was α-pinene, followed by β-caryophyllene. Other compounds present in lower amounts included limonene, longifolene, and 4-terpineol. Longifolene has been reported as a compound with particular interest for the insect vector of the pinewood nematode, namely to be used as an attractant in insect bait traps.[22]

Taking into account the identified volatiles, these forestry residues have potential to be used in insects' management strategies, namely by the extraction of repellent or attractive compounds and by their incorporation in controlled-release systems.

Volatiles from agrowastes (TW and WW) are included in Figure 2. For TW, 20 compounds were identified and semiquantified (∼80%), and 2-isobutyl-thiazole was the main volatile identified (Table S2), which is considered as a tomato flavor enhancer.[43] Some others were identified, and hex-(3Z)-enol, 2-isobutyl-thiazole, 2-octenal, and deca-(2E, 4E)-dienal were already identified by other authors in tomato samples.[16,44] Some differences in relation to the literature regarding volatile fraction composition may be attributed to the fact that volatiles emitted by fresh samples are different from those emitted by tomato residues. Thus, these samples may be used to extract volatile compounds (e.g., 2-isobutyl-thiazole) to enhance flavor-properties of tomato-based products and to improve organoleptic properties. However, the off-flavors have to be removed, in order to isolate the flavor-enhancing volatiles.

WW revealed the presence of 24 volatiles (∼80%) and denoted the presence of limonene and benzeneethanol, as the main volatiles. Limonene was already reported as an aroma component of wines,[45] while benzeneethanol was detected in high concentrations, in wines after distinct treatments.[46] Ethyl esters of octanoic and decanoic acids were also identified and correspond to flavor compounds that arise from the fermentation process.[45] Acetic acid, benzylalcohol, 3-methyl-1-butanol, and 3-methyl-1-butanol-acetate were also emitted from WW, in agreement with other authors.[45,46] In spite of being a residue, this sample may be important to extract relevant components of wine aroma, corresponding to an important source of flavor-enhancers compounds. Similarly to TW, some off-flavors have to be removed from the WW, namely 4-ethyl guaiacol (Table S2), that was already reported as a volatile phenolic off-flavor that results from the wine fermentation.[47]

Overall, the identified volatile compounds in all residues may be important as flavors in food and pharmaceutical industries, and in insects' management strategies.[12,41]

The main results of elemental and compositional analysis of the residues are included in Table 1, as well as other characteristics (pH, particle size, total solids, and volatile solids).

Both forestry residues presented higher C and O contents (>45%) than agrowastes (Table 1). On the contrary, the N contents of TW and WW were higher than those of PS and PB. Thus, agrowastes have lower C/N ratios when compared to both forestry residues. It is noteworthy that the C/N ratio of PS was more than 2-fold of the C/N ratio of PB (Table 1), due to the higher N content of PB as compared to PS. The results in Table 1 support the finding that biomass is highly variable, and these differences can be meaningful in similar materials and between different parts of the same plant species.[48,49] The C, H, and N contents of PS and PB were in agreement with literature values.[50]

The different stages of maturation of tomato, the edaphoclimatic conditions of production, and the applied industrial processes described in the literature[51] may
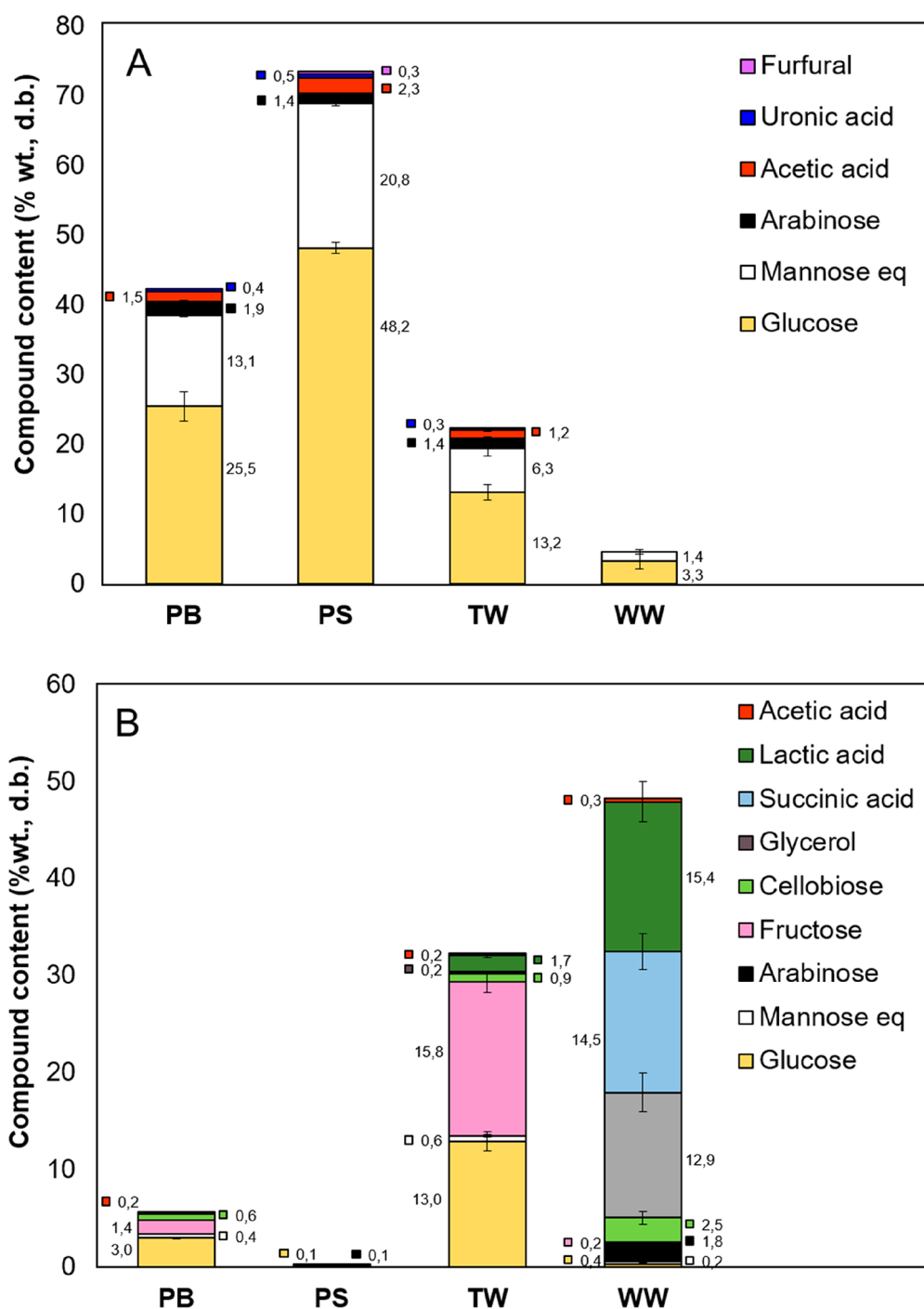
Figure 3. Carbohydrates, organic acids, alcohols, and carbohydrate degradation products detected and quantified by HPLC in the water-extracted agroforestry residues (A) and in the corresponding aqueous extracts (B).

contribute to some differences in the elemental composition, when compared with this work. The semirotten state of tomato fruits (TW) could also be responsible for those differences. However, another study[37] with tomato residues not processed and similar to TW from this study reported closer elemental compositions to those obtained in this work. The elemental analysis of WW is in agreement with the literature,[52−55] but some authors detected sulfur contents from 0.03%[55] up to 5.34%,[54] which may be explained by the different processing methods that were applied to obtain the winery wastes. The higher C/N ratios of forestry residues, when compared to the agrowastes, confer them a higher resistance to biological

degradation, since microorganisms need a proper balance of those elements.

Lignin comprises the sum of acid soluble and acid insoluble lignin, and the latter was the major fraction. WW showed the lowest value of acid soluble lignin content (0.8%), but the others have also presented a low value (1.3−1.8%). However, significant differences were observed in the acid insoluble lignin (Table 1), with PB presenting the highest content (32%), followed by PS (28%) and TW (18%). The total lignin content in each agroforestry residue was in agreement with the vast variability found in the literature (%wt, d.b.): 2.4 to 37% were reported for tomato wastes;[56−58] 4.2% for winery

Table 2. Total Phenolic Content and Antioxidant Activity in the Aqueous Extracts of the Four Agroforestry Residues

Raw material	PB	PS	TW	WW
Aqueous extract yield (%wt., d.b.)	21.6 ± 0.1	6.0 ± 0.5	52.5 ± 5.7	89.9 ± 4.6
Total phenolic content (mg GAE/g extract)	121.9 ± 7.4	438.1 ± 5.8	14.2 ± 1.4	23.6 ± 1.9
Antioxidant activity (IC$_{50}$, μg/mL)	51.9 ± 1.6	6.5 ± 0.6	1316.3 ± 6.2	386.5 ± 2.9

wastewater;[37] 29.5−31.5% for pine branches;[59,60] and 24.0−28.7% for pine stumps.[59] Differences in the amount of insoluble lignin between pine and tomato residues are due to the different composition of lignins. Pine lignin, almost exclusively derived from guaiacyl alcohols, has more trend to condensate in acid medium and to form an insoluble material. In the composition of nonwoody plants, other types of phenylpropane units are also present.[9] Concerning the results of this work, PB and PS are the most suitable for lignin recovery.

The highest cellulose and hemicellulose fractions were determined for PS with a total of 66.02%. Contrarily, PS presented the lowest water-soluble carbohydrates, as expected. The few available studies on pine stumps reported cellulose and hemicellulose contents of 36.4 and 28.2%, respectively,[59] slightly different from the results of the present study in which higher cellulose and lower hemicelluloses contents were observed. High cellulose and hemicelluloses fractions were found in PB, totalizing 37.88% of structural carbohydrates (cellulose *plus* hemicelluloses). The cellulose content in pine branches reported in the literature is in the range 20.7 to 32%,[60,61] while higher hemicellulose fraction was observed in other studies[61] compared to the present one (Table 1). Regarding the water-soluble carbohydrates, a higher content was determined in PB in comparison to PS. Structural carbohydrates content was lower in TW (19.85%) than in pine samples, consisting of 11.86% cellulose and 7.99% hemicelluloses, while the water-soluble carbohydrate content was the highest among the four agroforestry residues. These results were consistent with the information found in the existing literature, in which cellulose and hemicellulose contents of 7.7−16.2% d.b. and 7.5−15.7% d.b. were observed, respectively.[56,58] The lowest structural carbohydrates content was measured for WW. Figure 3A shows the compounds analyzed in the water-extracted residues by HPLC, derived from the acid hydrolysis of structural carbohydrates (cellulose and hemicelluloses), while the water-soluble compounds (analyzed in the aqueous extracts) are included in Figure 3B. The predominant carbohydrates in the water-extracted residues were glucose and mannose equivalents (Figure 3A). Arabinose, uronic acid, acetic acid, and furfural were found in minor quantities. TW and WW showed the higher diversity and quantity of compounds in the aqueous extracts, in comparison to PS and PB (Figure 3B). Glucose and fructose were the main water-soluble carbohydrates in TW, which is in accordance with other studies.[62,63] Glycerol and organic acids (lactic, succinic, and acetic acids) were the major compounds in the WW aqueous extracts, while a low quantity of carbohydrates was quantified, in agreement with the literature.[19] For WW, as received (before extraction and hydrolysis), other compounds were also detected: succinic acid; lactic acid; glycerol; ethanol; and arabinose (Figure S2). This is in accordance with Figure 3B and the high yield obtained for the WW aqueous extract (90%, Table 2). Furthermore, ethanol, acetic acid, and glycerol were also identified as volatiles by GC/MS (Table S2).

PS had the highest amount of fibers, followed by PB, TW, and WW (Table 1). This content is somewhat related to the respective carbohydrates content, confirmed by HPLC (Figure 3A).

Protein levels were higher in TW and WW, while minor quantities were determined for PB and PS (Table 1). TW revealed lower content when compared with the literature (6.38−16.4% d.b.).[62−64] This variability depends on the tomato variety, fruit maturity, and agronomic and environmental conditions during cultivation.[62,63] For WW, similar protein contents were reported in another study (1.73% d.b.) with winery wastewater from different wines production (red and white).[18] Regarding pine species, the protein content achieved in this work was lower than that indicated in the literature (1.35%, d.b.).[65] Nevertheless, a different wood part was analyzed, other than stumps or branches, which were targeted in the present study.

The highest lipids content was attained for PB, followed by TW, PS, and WW (Table 1). Lipids determined for both PS and PB are within the range of the values found in the literature: 1.6−5.1% of lipids in different parts of pine trees.[66] In this work, PB were used, which are mainly composed of needles that possess higher surface area than other parts of the tree (e.g., trunks and roots) and contain secretory structures able to release volatile oils. This explains the obtained value (4.11%), close to the maximum found in the literature. In tomato fruits, lipid contents from 1.45 up to 11.3% (d.b.)[63,64] were stated in other studies, which is in agreement with the result ∼2.3% (Table 1). The low lipid content measured in WW is in agreement with the results showed by other authors, 0.61−0.69% (d.b.), for winery wastewaters from red and white wines production.[18]

Aqueous Extracts Characterization. Aqueous extracts were characterized in terms of their total phenolic content and antioxidant activity. The corresponding results and the total yields are included in Table 2.

High extraction yields were obtained for WW (∼90%), while values ∼50% were obtained for TW. For tomato samples, aqueous extractions usually are not performed and literature mainly reports yield values for high pressure extractions, ultrasound-assisted extractions, or extractions with organic solvents.[17] Lower yields were achieved for both forestry residues, with values ∼22% for PB and ∼6% for PS. These findings are in agreement with results obtained by other authors, ∼18% yield for aqueous extracts of *Pinus densiflora* needles.[67] For pine stumps, the literature is scarce, and some authors have already reported very different yield values (∼15 to 85%) of aqueous extracts obtained from distinct *P. pinaster* wood samples.[68]

PS extracts showed the highest total phenolic content close to 440 mg GAE/g extract, and the highest antioxidant activity, denoted by the low IC$_{50}$, about 6 μg/mL (Table 2). This indicates phenolic compounds appear to be the main responsible components for the obtained antioxidant activity. High radical scavenging capacities have also been reported, in the literature, for hydrophilic extracts from *P. pinaster* wood

Table 3. Parameters of Combustion and Bioethanol and Biogas Production to Evaluate the Potential of Agroforestry Residues to Obtain Energy[a]

Raw material (d.b.)		PB	PS	TW	WW
HHV (MJ/kg)		21.7 ± 0.4	17.8 ± 1.8	19.8 ± 0.1	15.7 ± 0.3
$Y_{V,EtOH}$ (L/kg)		0.30 ± 0.02	0.47 ± 0.01	0.33 ± 0.00	0.06 ± 0.01
COD (gO$_2$/kg SV)		1376 ± 295	1185 ± 162	1419 ± 270	2509 ± 4
BD$_{anae}$ (%COD)		5	4	69	27
BMP$_{EXP}$ (NL CH$_4$/kg VS)[b]		22 ± 1	16 ± 2	341 ± 28	251 ± 6
BMP$_{th}$ (NL CH$_4$/kg VS)	MT_I	24[c]	17[c]	387[c]	157[c]
	MT_II	20[c]	16[c]	297[c]	115[c]
	MT_III	n/a	n/a	371	279
	MR_I	19[c]	13[c]	243	290
	MR_II	16[c]	13[c]	346	352

[a]d.b., dry basis; COD, total chemical oxygen demand; BD$_{anae}$, anaerobic biodegradability; BMP, biochemical methane potential. [b]Normal temperature and pressure (NTP) conditions. [c]BD$_{anae}$ corrective factor applied

samples.[68] Extracts from PB revealed the second highest antioxidant activity, IC$_{50}$ ∼ 52 μg/mL, with the total phenolic content being also the second highest value, >120 mg GAE/g extract. These interesting antioxidant values for PB are higher than those obtained by other authors for pine needles (373.7 ± 60.7 μg/mL),[67] and this difference may be attributed to the fact that PB also include wood in their composition, contrarily to needles (which only correspond to the pine leaves).

With respect to agrowastes, lower antioxidant potential was obtained, with IC$_{50}$ ∼400 and ∼1300 μg/mL for WW and TW, respectively. Also the phenolic contents were the lowest, 24 and 14 mg GAE/g extract for WW and TW, respectively. The obtained value of total phenolic content for WW is in agreement with the range 14−470 mg GAE/g extract, already reported for wine residue extracts.[69] For TW extracts, the values are in accordance with works carried out by other authors, with phenolic content in the range 5−39 mg GAE/g extract.[15,70] The extracts, namely from PS, have potential to be incorporated in food and/or pharmaceutical products due to their antioxidant properties.

Moreover, despite the fact that distinct raw materials were considered, a relationship between total phenolic content and antioxidant activity appears to exist as showed in Figure S3, in agreement with the literature.[70] This correlation is not linear, but lower IC$_{50}$ values (high antioxidant activity) corresponded to higher total phenolic contents, and the opposite for higher IC$_{50}$ values. This nonlinearity may be explained by different types of phenolic compounds that are present in the raw materials and by the presence of other nonphenolic compounds (e.g., carotenoids and fatty acids) with antioxidant activity.

Energy Production Potential. The main results regarding the potential of these residues for energy production (heat, bioethanol, and biogas) are presented in Table 3.

The HHV obtained for TW and WW were in agreement with the literature,[51,53,54] as well as the values observed for PS and PB.[50] The higher H of PB associated with the slightly higher C, and the lower O contributed to the superior HHV of PB as compared to PS (Tables 1 and 3). Forestry residues reflected the real calorific values of those materials, while the agrowastes had to be dehydrated in order to perform elemental analysis since the solid contents of these residues were 3 and 6 wt %, respectively. Therefore, based on calorific values of TW and WW, it would not be economically viable to evaporate such an amount of water in order to promote the combustion of them into thermal energy. However, these residues may be concentrated by partial evaporation in order to process them by anaerobic digestion into methane[71,72] or by hydrothermal liquefaction into bio-oil.[73] PB and PS can be handled directly as a whole using thermochemical technologies, such as pyrolysis[74] and direct gasification of lignocellulosic biomass.[75]

Bioethanol production through bioprocesses (enzymatic saccharification and fermentation) requires suitable carbon-rich substrates, along with the control of other relevant factors, such as temperature, substrate concentration, and pH.[12,76] The potential use of each residue for bioethanol production was assessed, considering the total sugars fraction in the residue (structural and water-soluble carbohydrates, shown in Figure 3) and the theoretical mass conversion yield of sugar to ethanol. The maximum ethanol volume that could theoretically be produced was evaluated and rated from the lowest to the highest: WW < PB < TW < PS (Table 3). According to this rating, WW is not suitable for sugar fermentation processes. Tomato pomace has been used as a single substrate or mixed with other food wastes to produce fermentable sugars or bioethanol,[58,64] and a recent study reported a product concentration of ∼16 g/L, achieving more than 60% of the theoretical yield.[77] Several studies on bioethanol production from woody biomass are available, mostly dedicated to hardwoods. Softwoods (such as pine trees) are also a target substrate. However, information regarding waste tree parts (particularly stumps) is still very scarce.[60] Contrarily to food wastes, the lignocellulose structure of woody biomass is more recalcitrant, and thus, severe pretreatments must be applied for lignin removal and carbohydrates recovery before enzymatic saccharification and fermentation processes.[60,78,79] Other authors determined low glucose and bioethanol yields (up to 55 and 48%, respectively) in enzymatic hydrolysis and simultaneous saccharification and fermentation (SSF) processes applied on pretreated pine branches and observed that the pretreatment had a significant effect on bioconversion yields.[60] PS presented in this work were already tested in SSF processes after a sequential pretreatment,[80] and high ethanol concentrations were produced (79 g/L) from a cellulosic pine stump pulp, with high sugar-to-ethanol conversion yield (97%). However, the global process yield (stump-to-ethanol conversion) was 44% of the maximum theoretical value, mainly due to low pulp yields obtained in the pretreatment (29%), showing the importance of pretreatment selection.

Biogas production through AD requires adequate control not only of the operating conditions but also of the substrate properties. The natural pH of the substrates is <5, and thus an

adjustment to the range of 6.5 to 7.5 must be done when assessed by AD.[81] Although all the substrates comprise high organic matter content (COD and VS), in the scope of biological processes, the assessment of the biodegradability is required. Thus, considering BD_{anae} reported in Table 3, TW is the most biodegradable substrate (69%) followed by WW (27%), while low biodegradability was observed for PB (5%) and PS (4%).

Table 3 shows that agrowastes exhibited the highest BMP, while forestry residues revealed a very low methane production (<25 NL CH_4/kg VS). Indeed, PS and PB were characterized by a very low BD_{anae}, probably due to the high content of total lignin.[82] Therefore, PS and PB require in general a pretreatment (e.g., mechanical, thermal, and chemical) before valorization by AD.[82,83] The valorization of these two substrates in a context of biorefinery could be interesting because after processing the material for the recovery of the value-added products, the biodegradability may be increased. Similar experimental BMP values are reported in the literature for TW,[71] PS, and PB,[84,85] whereas some studies indicated a higher BMP for WW.[72]

Since the experimental assessment of BMP involves a time-consuming procedure (more than 30 days), three theoretical models and two multivariate regression equations were applied to evaluate their ability to predict BMP values for further studies.[37] In the case of MT_I and MT_II, a corrective factor was applied based on the BD_{anae} of each substrate, since their biodegradability was not considered in those methods. Regarding MR_I and MR_II, this correction was also applied for PS and PB, because the models did not take into account the lignocellulosic nature of the substrates. All the models applied in this study showed a very good prediction capability of BMP for TW (Table 3). In fact, MR_II and MT_III are able to estimate the experimental value with a relative error of 2% and 9%, respectively. For WW, only MT_III and MR_I displayed an acceptable error, between 11% and 16%, respectively. For PS and PB, with the exception of MT_III, a very good BMP prediction was obtained for all the models. Overall, the models applied in this study exhibited good BMP estimation capacity for agrowastes and forestry residues.

In conclusion, all the residues may be applied in a biorefinery approach, based on their composition, main emitted volatiles, and potential for thermal energy, bioethanol, and biogas production. The main volatiles identified in PB and PS may be applied as repellents/attractants for insects' management strategies, while TW and WW revealed the emission of flavor-enhancers compounds. The aqueous extracts obtained from the four residues showed antioxidant activity, which was related to the content in phenolic compounds. Special attention should be given to the stump extract, which revealed the highest antioxidant properties, and may be used in food and pharmaceutical applications to increase shelf life of different products. The potential for biogas production was especially important for the agrowastes, while residues from *P. pinaster* can be recovered through thermo- and biochemical platforms to produce energy, biofuels (e.g., bioethanol), and value-added products from lignin, hemicelluloses, and cellulose fractions. The four agroforestry wastes are produced in abundance in the Portuguese territory, and based on these results, they should be valorized in the biorefinery context.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b03532.

> Equation of the anaerobic biodegradability; scheme of the residues sampling; carbohydrates content in the WW, as received; comparison of phenolic content vs antioxidant activity; models and methods for BMP prediction; and volatiles identification and quantification (PDF)

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Author Contributions

A. T. Portugal coordinated the activity of the MultiBiorefinery project, which is the basis of this work. M. E. M. Braga and M. C. Gaspar conceived the idea of analyzing these four residues in an integrative approach and organized the results. M. C. Gaspar wrote the manuscript with the support of coauthors. M. C. Gaspar and M. E. M. Braga carried out the analyses of lipids, fibers, and proteins, and M. C. Gaspar performed the volatiles experiments and antioxidant activity analyses. C. V. T. Mendes and R. Moreira performed the carbohydrates and lignin content analyses and determined the bioethanol production and combustion potentials. S. R. Pinela evaluated the biogas production and the total phenolic content. All authors contributed to the analysis and interpretation of the results. A. T. Portugal, M. G. V. S. Carvalho, and M. J. Quina reviewed and edited the text. All authors have read and approved the final version.

Notes

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