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Evaluation of the Phytomass Source for Composite Preparation

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ABSTRACT: The properties of lignocellulose materials from the trunk and bark of trees, and from agricultural sources were investigated by thermogravimetry (TG) and pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS). The goal was to learn which of the phytomass sources is the most accessible to dehydration and aldol reactions, and in this way could be considered suitable for composite preparation by the thermal pressing treatment. The bagasse second differential thermal analysis peak in air is at the highest temperature acceptable for intermolecular dehydration/crosslinking, and therefore we consider bagasse to be the most suitable candidate for composite preparation. From the TG results in air at 250°C, it follows that willow wood and bagasse are the most thermally resistant sources. The data obtained by Py-GC/MS analysis showed glycolaldehyde and acetic acid as dominant markers related to adhesion properties via aldol condensation. The detected sum amount of glyceraldehyde and acetic acid decreases in the order: beech wood > bagasse > acacia wood > sugar beet pulp, whereas the remaining species produced much less of it. By comparing results run at above conditions with composite preparation using the pressing thermal treatment at a temperature of 150°C and pressures up to 800 kPa, the suggested evaluation was examined for application on sugar beet residue. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

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INTRODUCTION

The potential for the preparation of composites from a wide range of phytomass residues is increasing.[1] To find the optimal source material for the preparation of composites by the thermal treatment method, it is necessary to study the thermal degradation of potential species and learn how the individual plant sources degrade. Wood species are different in cellulose, hemicellulose, and lignin content as well as in the structure of hemicellulose and lignin in softwoods and hardwoods. Several marker compounds have been identified in the mixtures of pyrolyzed wood materials which helps to quantify the mixture of products by pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS).[2–6] The results are different with pyrolysis temperature, species, and ingredients used during the manufacture process.[7] Besides the utilization of the trunk wood, there are fast-growing trees which might be used as whole trees with bark and roots as well as agricultural residues such as bagasse, sugar beet fiber, corn cobs (CC), or rapeseed residues (RSRs). These materials were previously studied with various techniques presenting mixtures mainly rich with lignin markers and less characteristic polysaccharide degradation products.[8–13] When isolated cellulose or starch samples were pyrolyzed, less aromatic markers were observed.[14,15] It is predicted that the different plant species and their components vary in their sensitivity to dehydration, β-elimination, condensation, and free-radical recombination processes owing to different plant cell wall compositions.[16] Additionally, there is the effect of oxygen on thermal processes.[17] On the basis of studies on xylan from beech wood (BW) as well as bagasse, the importance of hemicellulose dehydration as the main primary reaction was proven.[10,11,16] It is also important to see the lignin behavior. Lignin studied indirectly during wood pyrolysis of aspen (*Populus tremoloides*) in air environment was determined by TG and was completely degraded at temperatures lower than 600°C.[18]

In the present study, we used TG/differential thermal analysis (DTG) and Py-GC/MS to characterize wood, bark, and

agricultural by-products to understand the thermolysis and thermo-oxidation of these plant sources. The wood and bark samples were from both softwood and hardwood species and included samples from fast-growing hardwood trees. The goal was to learn how to use the obtained results to predict their behavior during the thermal exposure of a composite in a pressing machine.

MATERIALS AND METHODS

Materials

Specimens included both wood and bark samples from various hardwood and softwood trees. The softwood species included spruce (*Picea abies*) and pine (*Pinus sylvestris*). For hardwoods, beech (*Fagus sylvatica*) and oak (*Quercus robur*) were chosen. In addition, the following fast-growing hardwood plants were included: acacia (also known as black locust) (*Robinia pseudoacacia*), poplar (*P. nigra*), and willow (*Salix alba*). The agriculture residues included: CC (*Zea mays*); sugar beet fiber (SBF) (*Betula vulgaris*; Gemercukor, Rimavská Sobota, Slovakia); rapeseed (*Brassica napus*) residues after pressing procedure (PALMA Group, a.s., Bratislava, Slovakia); and bagasse (*Saccharum officinarum*; Davies Hamakua Sugar, P. O. Box 250, Paauilo, HI 96776, USA). The wood, bark, and CC samples were obtained from local sources. All samples were sieved to size particles of 0.5–1 mm. The names and abbreviations of the individual samples are listed in Table I.

Table I. Studied Samples and Their Holocellulose and Ash Content

Sample	Abbreviation	Holocellulose (wt. %)	Ash (wt. %)
Softwood species			
Pine wood	PW	73.28	0.29
Pine bark	PB	52.68	1.79
Spruce wood	SW	72.36	0.40
Spruce bark	SB	49.56	2.86
Hardwood species			
Beech wood	BW	67.94	0.34
Beech bark	BB	51.75	5.50
Oak wood	OW	81.51	0.34
Oak bark	OB	48.94	3.33
Fast -growing hardwood plants			
Acacia wood	AW	69.33	0.48
Acacia bark	AB	30.58	7.64
Poplar wood	PoW	68.95	0.55
Poplar bark	PoB	49.36	10.18
Willow wood	WW	83.55	1.77
Willow bark	WB	49.63	5.19
Agriculture residues			
Sugar beet fiber	SBF	61.91	3.57
Rapeseed residues	RSR	45.84	6.63
Corn cobs	CC	79.27	8.06
Bagasse	B	81.70	2.10

Methods

The holocellulose contents were determined as described previously.[19] Ash content was determined according to ASTM D1102-84 standard test method. TG measurements were conducted using inert (nitrogen) and oxidative (air) atmosphere in an upgraded (new electronics and software) Mettler Thermoanalyzer 2 instrument. The dynamic conditions were 10 K/min heating rate (linear temperature program), a 60-mL/min gas flow, ~60-min duration, ~30-mg sample weight, and a ceramic crucible.

Typically, a 150-μg sample was placed in a quartz tube and pyrolyzed with a CDS 5250 pyrolysis autosampler attached to a Thermo Trace GC Ultra/MD 800 GC/MS system. The samples were pyrolyzed at a temperature of 500°C for 10 s. Pyrolysis products were separated on a RTX 35 column (30 m, 0.32 mm id, 0.25 μm) with He 4.6 as carrier gas (1.5 mL/min) and identified by interpretation of their EI mass spectra and comparison to NIST 2002, Wiley, and NBS electronic libraries, as well as to the literature data. The pyrolysis interface was kept at 300°C and the GC/MS interface kept at 280°C. The GC was operated in split mode at 20 mL/min and programmed from 50°C (2 min) to 300°C (10 min) at a rate of 20°C/min. The mass spectrometer was operated in EI mode (70 eV) at a source temperature of 200°C.

RESULTS AND DISCUSSION

In Table I, the results for holocellulose and ash content are summarized. Table II lists the dynamic thermogravimetry (TG) data. The residues at 105°C in the inert nitrogen environment (Table II) represent the dry weights of the individual samples. The next DTG maxima of individual samples at higher temperature were in the following increasing order: beech bark (BB; 155°C) < BW (158°C) < CC (160°C) = oak wood (OW; 160°C) = poplar wood (PoW; 160°C) = pine bark (SB; 160°C) = spruce bark (160°C) < spruce wood (SW; 161°C) < pine wood (PW; 162°C) < acacia wood (AW; 164°C) = willow bark (WB; 164°C) < willow wood (WW; 165°C) < oak bark (OB; 166°C) = bagasse (B; 166°C) < SBF (169°C) = RSRs (169°C) = acacia bark (AB; 169°C) < poplar bark (PBB; 181°C). These are just minor peaks followed by another minor DTG peaks at 188°C (BB) < 202°C (AB) < 204°C (BW) = 204°C (WB) = 204°C (OW) < 207°C (SB) = 207°C (SW) = 207°C (OB) = 207°C (PB) = 207°C (SBF) < 210°C (AW) 210°C (RSR) < 211°C (WW) < 212°C (PW) < 215°C (CC) < 216°C (B) < 278°C (PBB) < 290°C (PWW). When comparing the first group of maximums with the second group, the differences between the temperatures of the DTG peaks for individual samples in both groups are not so dramatic. The exceptions are pine bark and PW with DTG peak temperatures listed in the second group, which are evidently the temperatures of main depolymerization process.

It is known that the first DTG maximum for BW is related to xylan dehydration with maxima determined on isolated (4-*O*-methyl-D-glucurono)-D-xylan at 158, 185, 220, and 325°C.[16] The main maximum at 325°C is owing to depolymerization splitting of glycosidic bonds, but the first three minor maxima are related to inter and intramolecular dehydration. Also, the first two DTG maxima of SBF at 169 and 207°C are also probably related to arabinan dehydration with the further peaks at 244, 283, and 319°C. Analogically, the dehydration is first reaction observed during thermal degradation of CC as

Table II. Dynamic TG Data of Studied Samples (weight %)

		Temperature (°C)															
Sample	Environment	105	250	275	300	325	350	375	400	425	450	475	500	525	550	575	600
Softwood species																	
PW	Nitrogen	85	80	77	72	63	51	33	29	27	25	24	23	22	21	20	20
	Air	86	81	77	69	54	40	35	31	26	20	14	8	4	4	4	4
PB	Nitrogen	88	81	78	74	68	59	50	47	44	41	39	38	37	36	35	34
	Air	87	79	75	68	56	48	43	38	32	26	20	14	8	4	3	3
SW	Nitrogen	71	61	59	55	47	37	27	25	24	23	22	21	20	20	20	20
	Air	78	72	69	61	46	34	30	26	21	16	10	4	2	2	2	2
SB	Nitrogen	90	82	78	73	67	59	50	47	44	42	40	38	37	36	35	34
	Air	92	84	79	72	62	54	48	42	36	29	23	17	12	8	6	6
Hardwood species																	
BW	Nitrogen	92	89	86	77	67	55	37	34	32	31	30	29	28	27	26	26
	Air	90	85	78	63	44	34	29	24	19	13	7	2	1	1	1	1
BB	Nitrogen	95	88	84	77	70	62	52	49	46	44	42	40	38	37	36	36
	Air	91	82	75	65	55	47	42	37	32	27	21	15	10	7	7	7
OW	Nitrogen	91	85	81	72	62	48	33	30	28	26	25	24	23	22	21	21
	Air	93	86	77	62	45	36	31	26	20	14	8	2	1	1	1	1
OB	Nitrogen	93	84	79	73	67	59	50	47	44	41	39	37	35	34	33	32
	Air	93	83	77	68	59	49	43	38	33	28	21	15	11	8	8	8
Fast -growing hardwood plants																	
WB	Nitrogen	96	88	84	78	71	62	53	49	45	42	40	38	37	36	35	34
	Air	95	86	80	71	60	51	45	39	33	27	21	16	12	10	10	10
AB	Nitrogen	97	87	83	77	69	57	47	44	42	40	38	36	34	33	32	32
	Air	96	85	79	70	59	51	47	43	39	35	31	25	21	17	13	11
PoB	Nitrogen	97	88	83	77	70	60	51	48	46	44	42	39	37	36	35	35
	Air	95	85	79	69	59	52	48	44	40	35	28	22	17	14	13	13
WW	Nitrogen	96	91	86	77	63	42	35	33	31	29	28	27	26	25	24	24
	Air	97	91	80	61	48	40	34	28	22	16	11	6	4	4	4	4
AW	Nitrogen	94	90	86	78	69	56	40	37	35	34	33	32	31	30	29	29
	Air	93	87	79	66	47	38	33	28	23	18	12	6	2	1	1	1
PoW	Nitrogen	92	87	83	75	66	53	35	30	28	26	25	24	23	22	21	20
	Air	94	89	81	68	48	39	33	27	21	15	8	2	1	1	1	1
Agriculture residues																	
SBF	Nitrogen	96	80	72	64	55	47	43	40	37	34	31	28	25	22	19	17
	Air	94	77	69	60	50	42	38	35	31	27	24	20	15	11	7	4
RSR	Nitrogen	98	84	79	73	65	57	52	48	45	42	40	39	38	37	36	36
	Air	97	81	75	68	61	56	53	50	47	44	41	38	35	32	28	24
CC	Nitrogen	97	91	84	72	61	47	43	41	39	37	36	35	34	33	32	32
	Air	95	87	72	56	46	40	35	29	23	17	12	9	8	8	8	8
B	Nitrogen	96	89	84	71	55	41	36	32	28	23	19	14	10	6	4	3
	Air	96	89	83	71	51	40	35	30	25	19	14	10	6	5	4	3

represented by minor peaks at 160 and 215°C.[13] Demethoxylation concerning uronic acids is only a minor reaction, as uronic acid carboxyls are linked to lignin.[20] Demethoxylation of lignin producing methanol also takes place more intensively at the above-mentioned temperatures.[21] The differences between individual species are expressed by differences in DTG maxima.

When comparing the amounts of residues at 250°C in inert nitrogen environment, the order is WW (91%) = CC (91%) > AW (90%) > B (89%) = BW (89%) > PoB (88%) = WB (88%) = BB (88%) > PoW (87%) = AB (87%) > OW (85%) > RSR (84%) > OB (84%) > SB (82%) > PB (81%) > PW (80%) = SBF (80%) > SW (61%). These results indicate

relative good thermal stability of most of the materials and the intermolecular dehydration on up to 10% of the available hydroxyl groups.

For the air environment results, we ascribed the order of first group of DTG maxima in comparison to those observed in nitrogen to changes in dehydration. The maxima in order of increasing temperature are SW (154°C) < RSRs (158°C) < OW (160°C) = pine bark (160°C) < PoW (161°C) < CC (162°C) = AW (162°C) = PW (162°C) = spruce bark (162°C) < SBF (164°C) = WB (164°C) < WW (170°C) = BW (170°C) < bagasse (172°C) < BB (175°C) = OB (175°C) < AB (176°C) < PBB (186°C). The second group of DTG minor peaks follows in order: PW (200°C) < SBF (203°C) < BB (205°C) = SW (205°C) = CC (205°C) < OB (208°C) = PoW (208°C) = WB (208°C) = OW (208°C) = spruce bark (208°C) < pine bark (209°C) < AW (210°C) < WW (212°C) = AB (212°C) < BW (214°C) = RSR (214°C) < bagasse (215°C) < PBB (281°C). Both groups of peaks are again in a close range of temperatures with exception of PBB, with a DTG peak owing to hemicellulose depolymerization at 281°C. Under both inert and oxidative conditions, the bagasse sample has the lowest first DTG peak, which is at a lower temperature than for all other species. On the other side, bagasse has an additional peak at 166 or 172°C in both environments, which is also within the corresponding range of first group DTG peaks. That is why we do not consider the first DTG peaks at 119 or 115°C observed in inert and oxidative conditions as crucial for sample evaluation. As DTG peaks for all the samples are at such a close range of temperature, all the samples could fulfill the expectations for dehydration requirements. As bagasse second DTG peak in air environment is at the highest temperature acceptable for intermolecular dehydration/crosslinking, we consider bagasse as a most suitable candidate for composite preparation under thermal pressing conditions.

When comparing the amount of residues in air at 250°C, the values are decreasing in order: WW (91%) > B (89%) = PoW (89%) > AW (87%) = CC (87%) > OW (86%) = WB (86%) > PoB (85%) = AB (85%) = BW (85%) > SB (84%) > OB (83%) > BB (82%) > PW (81%) = RSR (81%) > PB (79%) > SBF (77%) > SW (72%). The most stabile sample is WW, which resulted in the same residue amount in both environments. With only marginal difference from WW, bagasse is again near the top of the list. This is in agreement with DTG peak evaluation. The least thermally stabile sample is SW in both environments.

As during the pressing of the materials, the reactions observed with TG/DTG at higher temperatures will take place at lower temperature at elevated pressure. Thus, the comparison of residue amounts at 500°C might give additional information. The pyrolysis was also performed at this temperature and under inert environment. The amount of residues observed in inert environment decreases in order: BB (40%) > PoB (39%) > PB (38%) = SB = WB > OB (37%) >AB (36%) > CC (35%) > AW (32%) > BW (29%) > SBF (28%) > WW (27%) > OW (24%) > PW (24%) > PW (23%) > SW (21%) > B (14%). At the presence of air at 500°C, the values of residues are decreasing in order: RSR (38%) > AB (25%) > PoB (22%) > SBF (20%) > SB (17%) > WB (16) > BB (15%) = OB > PB (14%) > B (10%) > CC (9%) > PW (8%) > WW (6%) = AW > SW (4%) > PoW (2%) = OW =BW. Although in inert environment BB is the most resistant, the most resistant in the presence of air is the RSR sample. We do not consider the obtained results affected by the ash contents of sample, as at 500°C there is some lignin residue present. In air environment, RSR was the most thermally stable sample at 500°C. Hence, we can conclude that from the TG/DTG results the best source is WW and bagasse, while also poplar, AW, and CC might also be suitable for the application.

The processes that take place at temperatures above 200°C are degrading the macromolecular structure to small volatile molecules, which could be analyzed by Py-GC/MS (Table III). The first degradation products related to the above DTG peaks are water, methanol, carbon dioxide, CO, formaldehyde, formic acid, acetone, and acetic acid.[16] When the pyrolysis takes place at 500°C, water, CO_2, CO, and some other gaseous products formed at much lower temperature could not be well quantified. Thus, the dehydration could not be evaluated by Py-GC/MS directly. On the other hand, some compounds present in thermolysis products could be considered important adhesive precursors that dramatically affect the composite formation during pressing treatment at elevated temperatures owing to condensation reactions. The main candidate for the condensation process is glycolaldehyde which readily undergoes aldol condensation under alkaline conditions.[22] This compound is also the predominant quantifiable product. For oak species, the glycolaldehyde and acetic acid were overlapping owing to their high content in the mixture. All the acids are enhancing the aldol condensation, as it is observed under both acidic and alkaline conditions. Acids are also important dehydration markers. The mechanism under thermal treatment might be condensed to cyclohexan structures, which could be further transfered into three-dimensional aromatic macromolecules.[23] We assume that during the pressing of material at 150°C and pressures up to 800 kPa, the retro-aldolization and subsequent aldol condensation do not progress so far that browning of the sample takes place. This was proven by FTIR spectroscopy.[24]

When expressed in relation to guaiacol amount instead of peak area, the GC response of glycolaldehyde is almost 21 times larger than for guaiacol (Table III) although the changes in area of guaiacol within individual samples ranged from 0.13 to 1.09%. For wood trunk samples, this compound seems to be a significant standard for comparison to other products with yields higher than 1% of the total GC peaks area. Besides acetic and pyruvic acid, pyruvic acid methyl ester, methyl acetate as unspecific polysaccharide markers, there are 5-hydroxymethyl-2-furaldehyde (HMF) and 2-furaldehyde as cellulose and hemicellulose markers and dehydration products. Other cellulose markers are 5-hydroxymethyltetrahydrofuranone, 2,5-dihydro-5-methylfurane-2-one, dihydropyran, 5,6-dihydropyrane-2,5-dione, and 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one (HDPO).[8] There are four unknown compounds with retention times (RTs) at 5.30, 5.67, 6.38, and 6.8 min that probably are of carbohydrate origin. The first unknown (m/z = 114; $C_6H_5O_3$ or

Table III. Py-GC/MS Data of Wood Trunk Species as well as the Ratios of Detected Products[a]

Compound (RT)[b]/sample	Pine	Spruce	Beech	Oak	Willow	Acacia	Poplar
Pyruvic acid (1.74)	8.491	5.855	12.963	2.597	1.138	46.639	6.155
Acetic acid (1.97)	8.768	7.724	65.106	0[c]	5.340	3.762	21.759
Glycolaldehyde (2.08)	20.781	20.410	36.761	37.355	11.321	45.530	20.140
Methylacetate (2.66)	5.313	4.015	8.808	5.028	5.540	4.664	3.858
Hydroxyacetone (3.74)	3.897	3.230	10.530	3.363	1.931	4.859	5.791
Pyruvic acid methylester (4.01)	3.412	2.349	4.432	1.405	1.074	1.852	3.824
Propanal (4.18)	1.773	1.551	4.047	2.997	3.611	3.071	2.084
2-Furfural (4.40)	3.187	1.459	5.753	2.870	1.430	3.268	3.046
HMTHF[d] (5.21)	1.030	1.033	4.865	0.764	0.254	0.650	4.029
Unknown (5.3)	1.151	1.052	2.836	1.854	2.252	1.728	1.545
Unknown (5.67)	1.444	0.584	3.163	0.813	0.534	1.235	2.309
Dihydropyran (5.72)	0.856	0.832	2.497	1.159	1.108	1.169	1.071
DHPD[e] (6.04)	0.826	0	1.683	0.600	0.364	0.708	1.973
HDPO[f] (6.12)	5.014	3.426	12.894	2.259	0.628	3.430	10.304
Unknown (6.38)	2.073	1.155	0.594	1.040	0.569	1.191	0.993
Guaiacol (6.68)	1	1	1	1	1	1	1
Unknown (6.80)	1.772	1.444	2.474	2.049	1.501	2.239	2.354
Pentanal (7.26)	1.971	2.328	5.504	4.181	5.501	3.316	2.588
Methylguaiacol (7.42)	1.588	2.016	1.835	0.644	0.404	0.690	1.074
Dianhydropentose (7.79)	3.348	0	0	0.198	0.223	0.207	0.252
HMF[g] (8.13)	2.655	0.931	3.521	1.703	0.304	0.901	2.502
Vinylguaiacol (8.38)	3.264	2.271	1.084	1.174	1.129	1.287	1.505
Syringol (8.86)	0	0	29.032	3.828	2.979	3.407	1.586
TPG[h] (9.27)	0.652	3.503	5.993	6.156	2.246	8.707	4.132
Vinylsyringol (10.16)	1.843	2.271	4.785	5.963	4.524	5.359	3.783
TPS[i] (10.92)	0.652	0	5.993	6.156	2.246	8.707	4.133
Propenylguaiacol (11.35)	10.324	12.344	3.647	3.047	2.622	4.717	6.034
Prop-2-enal-syringol (12.68)	0	0	2.425	0.536	0.533	1.700	2.030
trans-Sinapyl alcohol (12.77)	0	0	1.841	0.636	1.121	3.270	1.149

[a]Area of GC peak in relation to amount of guaiacol present., [b]Retention time in minutes., [c]Acetic acid and glycolaldehyde peaks were overlapped and only the sume of both markers could be determined., [d]Hydroxymethyltetrahydrofuranone., [e]5,6-Dihydropyrane-2,5-dione., [f]4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one., [g]5-Hydroxymethylfuraldehyde., [h]*trans*-2-Propenylguaiacol., [i]*trans*-2-Propylsyringol.

$C_6H_{10}O_2$) might be related to 3-methylpyran-2,4-dione or unknown ascribed by Py-GC/MS on cellulose.[14] Guaiacol's RT was 6.68 min, which is not interacting with unknown compound at 6.80 min with $m/z = 128$. This degradation product could belong to a furane-related structure (C_8O_2). There are no references for this compound, which might be in two isomers having oxygen atoms linked in different way. The last known pentose marker observed on xylan is dianhydropentose ($m/z = 114$; RT = 7.79 min; area, 1.68%)[10], formed in more than three times greater amount in comparison to guaiacol. The rest of the compounds listed in Table III for PW sample are lignin markers: methylguaiacol (0.80%), vinylguaiacol (area, 1.64%), vinylsyringol (0.93%), tetra-2-propenylsyringol (0.33%), and acetylsyringol (1.35%).

The results for SW are similar to pine sample except for smaller amounts of 2-furaldehyde and HMF and the absence of dianhydropentose. It is owing to lower amount of xylan in the cell walls. For hardwood samples (beech and oak), much more of glycolaldehyde was observed. For beech, a high amount of syringol was observed while this compound was not observed in pine and SW. Also for beech, the amount of HDPO was very high and dianhydropentose was absent. As with syringol, prop-2-enol-syringol and *trans*-sinapyl alcohol were present in BW and also absent in pine and spruce. Acetic acid was absent and much less HDPO and syringol were present in OW than in beech, whereas vinylsyringol in OW was the highest of all samples listed in Table III. Glycolaldehyde was the predominant marker for fast-growing acacia although it varied considerably between individual samples owing to inaccuracy in GC determination as the result of separation problems at high concentrations. Glycolaldehyde value for acacia was the greatest among the trees and likewise the smallest for willow. For the rest of the markers; vinylsyringol, *trans*-2-propenylsyringol, propenylguaiacol, prop-2-enal-syringol, and *trans*-sinapyl alcohol were high in

Table IV. Py-GC/MS Data of Wood Bark Species Quantified as the Ratios of Detected Products[a]

Compound (RT)[b]/Sample	Pine	Spruce	Beech	Oak	Willow	Acacia	Poplar
Pyruvic acid (1.74)	3.285	2.775	3.213	6.651	1.386	1.099	2.169
Acetic acid (1.97)	2.480	4.996	14.142	16.059	0[c]	0[?]	10.504
Glycolaldehyde (2.08)	5.525	4.288	4.525	12.864	13.137	11.237	2.867
Methylacetate (2.66)	1.256	2.746	4.223	8.215	2.042	1.424	2.594
Hydroxyacetone (3.74)	0.557	0.801	1.851	2.023	0.815	0.223	1.281
Pyruvic acid methylester (4.01)	0.938	0.738	0.940	2.163	0.060	0.200	0.756
Propanal (4.18)	2.261	1.202	0.981	3.076	0.638	0.425	1.091
2-Furfural (4.40)	5.113	2.030	1.794	5.680	1.109	0.929	1.375
HMTHF[d] (5.21)	0.598	0	0	0.549	0	0	0
Unknown (5.3)	0.672	0.077	0.810	2.145	0.553	0.373	0.723
Unknown (5.67)	1.607	0.589	0.418	1.289	0.309	0.258	0.482
Dihydropyran (5.72)	0.419	0.472	0.407	1.237	0.251	0.145	0.338
DHPD[e] (6.04)	0.570	0.402	0.280	1.042	0.196	0.104	0.264
HDPO[f] (6.12)	3.996	1.508	0.958	1.756	0.499	0.225	0.932
Unknown (6.38)	1.294	1.103	0.490	4.493	0.833	0.841	0.728
Guaiacol (6.68)	1	1	1	1	1	1	1
Unknown (6.80)	1.047	0.439	0.575	1.880	0.169	0.067	0.509
Pentanal (7.26)	0.374	0.609	1.185	2.744	0.838	0.447	1.161
Methylguaiacol (7.42)	2.684	0.972	0.901	1.250	0.222	0.177	0.586
Dianhydropentose (7.79)	4.954	2.177	2.020	8.679	1.379	1.481	1.585
HMF[g] (8.13)	3.041	0.861	0.365	7.565	0.438	0.252	1.021
Vinylguaiacol (8.38)	4.488	1.176	1.291	0.681	1.891	0.890	0.991
Syringol (8.86)	0	0.292	3.011	1.593	0.638	1.043	0.771
TPG[h] (9.27)	2.462	1.061	1.554	0.490	0.900	0.562	1.152
Levoglucosan (10.15)	3.066	6.317	0	0	1.007	0	0
Vinylsyringol (10.16)	0	0	2.215	1.164	0.688	0.453	0.960
TPS[i] (10.92)	0	0	3.582	0.736	0.668	0.468	0.982
trans-Coniferyl alcohol (11.34)	0	01.386	1.529	0	0	0	1.109
Propenylguaiacol (11.35)	1.541	0.537	0	0.442	1.040	0.273	0
Prop-2-enal-syringol (12.68)	0	0	0.496	0.136	0.063	0	0.167
trans-Sinapyl alcohol (12.77)	0	0	0.218	0	0	0	0.079

[a]Area of GC peak in relation to amount of guaiacol present., [b]Retention time in minutes., [c]Acetic acid and glycolaldehyde peaks were overlapped and only the sume of both markers could be determined., [d]Hydroxymethyltetrahydrofuranone., [e]5,6-Dihydropyrane-2,5-dione., [f]4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one., [g]5-Hydroxymethylfuraldehyde., [h]*trans*-2-Propenylguaiacol., [i]*trans*-2-Propylsyringol.

all three fast-growing hardwoods, whereas the highest in acacia. Additionally, the second highest peak for HDPO was for poplar while the highest HDPO peak for all the trees was for BW. For the chosen trunk wood species, the order of decreasing glycolaldehyde formation is acacia > oak > beech > poplar = pine = spruce > willow. In some cases, the glycolaldehyde and acetic acid had GC areas that are overlapping. Both of these compounds are responsible for aldol condensation and acetic acid also affects the dehydration. Thus, the combined GC areas for glycolaldehyde and acetic acid were examined. The order of decreasing combined GC areas was BW > AW > PW > OW > PW > SW > WW.

The bark samples (Table IV) contained smaller amounts of acetic acid with glycolaldehyde again as a dominant marker as also observed on the wood trunk samples. Besides, 2-furfural, dianhydropentose, levoglucosan, and HMF were also the most intense hemicellulose and cellulose markers for pine bark. The lignin presence was demonstrated by vinylguaiacol, guaiacol, TPG, and propenylguaiacol, but no syringol derivatives were present. A similar situation was observed for spruce bark with levoglucosan as a predominant marker. The predominant polysaccharide markers for BB were acetic acid, glycolaldehyde, and methylacetate but levoglucosan was absent. For BB, both guaiacol and syringol markers were present. The intensities of polysaccharide markers for OB decreased in order: acetic acid > glycolaldehyde > dianhydropentose > methylacetate > HMF > pyruvic acid > 2-furfural > unknown with 6.38 min RT > pentanal > unknown with 5.30 min RT. The lignin markers were in minority with syringol and vinylsyringol close to

Table V. Py-GC/MS Data of Agricultural Byproducts Quantified as the Ratios of Detected Products[a]

Compound (RT)[b]/Sample	SBP	RSR	CC	B
Pyruvic acid (1.74)	8.998	0	7.749	15.100
Acetic acid (1.97)	45.459[c]	22.208	12.235	0[c]
Glycolaldehyde (2.08)	-[c]	2.629	24.481	81.135[c]
Methylacetate (2.66)	9.393	9.563	5.678	3.689
Hydroxyacetone (3.74)	3.620	1.474	2.350	5.878
Pyruvic acid methylester (4.01)	2.797	3.336	2.125	2.614
Propanal (4.18)	4.599	3.128	4.441	2.111
2-Furfural (4.40)	7.946	3.130	1.564	15.836
HMTHF[d] (5.21)	0.890	0	0	3.912
Unknown (5.3)	2.796	2.517	3.485	1.953
Unknown (5.67)	1.647	5.890	0.550	7.832
Dihydropyran (5.72)	1.378	2.160	1.630	1.081
DHPD[e] (6.04)	1.327	1.561	0	0
HDPO[f] (6.12)	0.939	2.067	0	0
Unknown (6.38)	6.643	10.489	0.880	0
Guaiacol (6.68)	1	1	1	1
Unknown (6.80)	1.938	1.725	1.675	0.306
Pentanal (7.26)	4.288	2.461	4.052	2.547
Methylguaiacol (7.42)	0.866	2.137	0	0.348
Dianhydropentose (7.79)	17.049	14.828	0.333	2.480
HMF[g] (8.13)	6.374	3.087	0	11.270
Vinylguaiacol (8.38)	5.141	1.247	3.041	19.594
Syringol (8.86)	0	2.546	1.674	0.620
TPG[h] (9.27)	0	0	0	2.034
Levoglucosan (10.15)	1.280	0	0	0.903
Vinylsyringol (10.16)	0	62.13	0.536	2.041
TPS[i] (10.92)	0	0.713	0	2.817
trans-Coniferyl alcohol (11.34)	0	0.324	0	1.456
Propenylguaiacol (11.35)	0	0	0	0
Prop-2-enal-syringol (12.68)	0	0.324	0	0.305
trans-Sinapyl alcohol (12.77)	0	0	0	0

[a]Area of GC peak in relation to amount of guaiacol present., [b]Retention time in minutes., [c]Acetic acid and glycolaldehyde peaks were overlapped and only the sume of both markers could be determined., [d]Hydroxymethyltetrahydrofuranone., [e]5,6-Dihydropyrane-2,5-dione., [f]4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one., [g]5-Hydroxymethylfuraldehyde., [h]*trans*-2-Propenylguaiacol., [i]*trans*-2-Propylsyringol.

guaiacol response. For WB, glycolaldehyde was the predominant marker with one order of magnitude less of methylacetate, pyruvic acid, 2-furaldehyde, dianhydropentose, and levoglucosan. For lignin markers, only vinylguaiacol and propenylguaiacol had more intense response than guaiacol. Glycolaldehyde was also the predominant marker for acacia. The other polysaccharide markers present were dianhydropentose > methylacetate, with levoglucosan absent. From lignin markers, none was more intense in acacia than guaiacol. PBB was represented by acetic acid as the predominant product with methylacetate, pyruvic acid, and pentanal as less intense peaks. In some cases like willow and acacia, glycolaldehyde was overlapping with acetic acid. As a lignin marker for PBB, only TPG was more intense than guaiacol. The combined areas of glycolaldehyde and acetic acid for bark samples decreased in the following order: OB > BB > PoB > WB > AB > SB > PB.

The Py-GC/MS data for agricultural by-products are summarized in Table V. For SBF, acetic acid and glycolaldehyde were again overlapping each other and only the sum of the two could be determined. The other observed compounds were dianhydropentose, methylacetate, pyruvic acid, 2-furaldehyde, HMF, vinylguaiacol, propanal, pentanal, and unknowns at 5.30, 6.80, and 5.67 min RTs. The intensity of vinylguaiacol was five times that for guaiacol with no other lignin markers observed. The RSR sample markers decreased in order: vinylsyringol, acetic acid, dianhydropentose, unknown at 6.38 min, methylacetate, unknown at 5.67 min, pyruvic acid methylester, 2-furaldehyde, propanal, HMF, pentanal, syringol, unknown at 5.30 min, dihydropyran, HDPO, unknown at 6.80 min, DHPD, hydroxyacetone, and vinylguaiacol. These were all more intense than guaiacol. This sample is the only case where the lignin marker was the predominant marker of all the products determined. CC

sample was represented by glycolaldehyde marker, followed by acetic acid, pyruvic acid, methylacetate, propanal, pentanal, unknown at 5.30 min, vinylguaiacol, unknown at 6.80 min, and syringol. For this agricultural by-product, dianhydropentose and HMF were less intense than guaiacol. Also for bagasse, the glyceraldehyde and acetic acid GC peaks were overlapped. The other degradation products were vinylguaiacol, 2-furaldehyde, pyruvic acid, HMF, unknown at 5.67 min, hydroxyacetone, hydroxymethyltetrahydrofurane, propanal, pentanal, dianhydropentose, TPS, vinylsyringol, TPG, unknown at 5.30 min, *trans*-coniferyl alcohol, and dihydropyran. Bagasse contained more lignin markers than the other agricultural by-products. It is also evident that bagasse produces the greatest amount of glyceraldehyde from all studied species. In this relationship, sugar beet and CC are less effective than bagasse, whereas RSR showed vinylsyringol as the predominant marker. Hence, the amount of aldol reaction precursors expressed for agricultural residue as a sum of glycolaldehyde and acetic acid decreased in order: bagasse > sugar beet pulp > CC > rape seed residues.

When we add together the amounts of glycolaldehyde and acetic acid for each of the studied samples, the decreasing order is BW > bagasse > AW > sugar beet pulp > PW > OW > CC > PW > OB > SW > RSRs > BB > WW > PBB > WB > AB > spruce bark > pine bark. Therefore, BW and bagasse are the strongly prefered sources according to the abundance of aldol condensation and dehydration markers observed by Py-GC/MS.

CONCLUSIONS

Based on the assumption that dehydration and aldol condensation are the most important reactions in the thermal pressing of panel composites, both analytical methods (TG and Py-GC/MS) identified bagasse as the optimal source of phytomass residue for this application. This conclusion is supported by the DTG peak of bagasse related to intermolecular dehydration/crosslinking at the highest temperature from all studied samples. According to the amount of residue at 250°C in air environment, only WW exhibited slightly better thermal stability than bagasse. From only the Py-GC/MS results, BW was recognized as a better source of phytomass for the mentioned application. Paralleling these findings, the preparation of composite panels from SBF was investigated.[24] SBF was evaluated as the fourth best according to Py-GC/MS and the second least stabile sample according to TG at 250°C in air environment. On the other hand, SBF was judged as the second best source according to the second DTG peaks order at 203°C related to intermolecular dehydration/crosslinking of arabinan.

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