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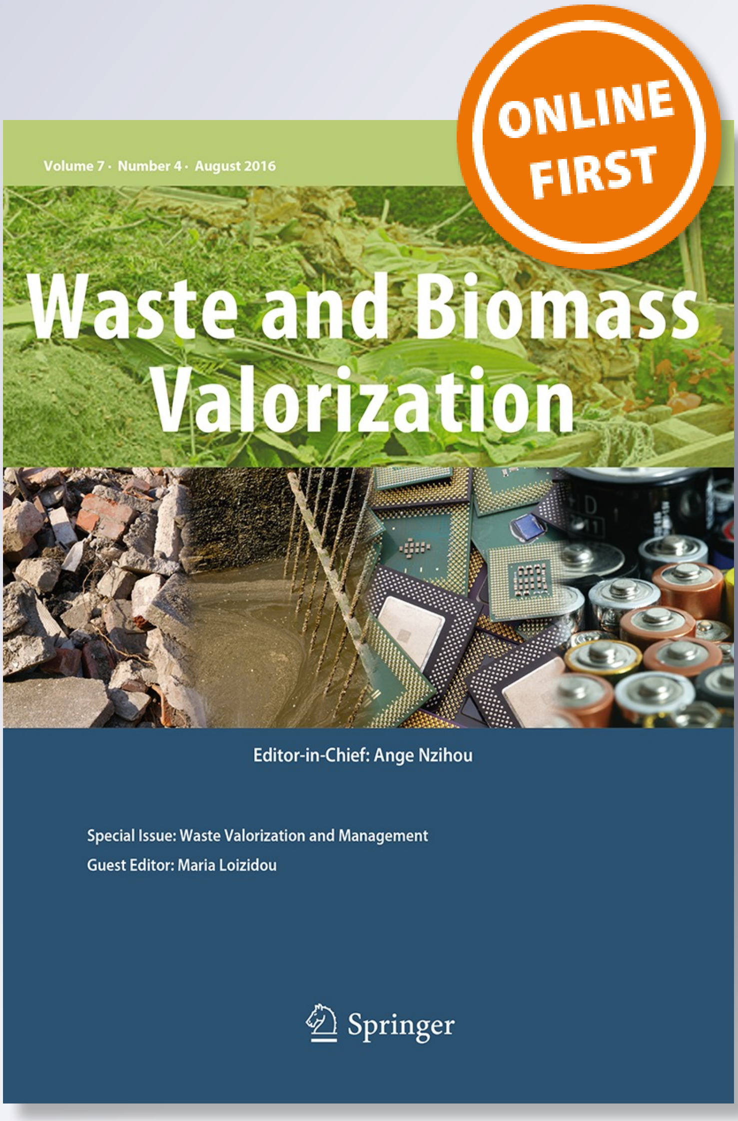

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ORIGINAL PAPER

Production of Sugars from Wood Waste Materials Via Enzymatic Hydrolysis

Manuel Raul Pelaez-Samaniego[1,2] · **Karl R. Englund**[1]

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Abstract Wood waste residues (WWRs) are abundant feedstocks for producing energy and fuels. However, using these materials is in part hindered by the lack of uniformity in properties and presence of contaminants. This work aimed at determining the potential of WWRs for sugars production via enzymatic hydrolysis. Pretreatment of four WWR samples was conducted using a mild bisulfite process at 165 °C and 75 min (SPORL process) and particles that passed through a 25 mm mesh screen and were retained by a 12.5 mm mesh screen. The yield from the pretreatment was up to 79 %. Carbohydrates in pretreated materials ranged from 66 to 76 mass%. Results of the enzymatic hydrolysis indicated that the sugar yields (varying from 49 to 60 %) depend on the material. Sugar yields varied from 56 to 66 %. These findings suggest that, although the total yields are relatively lower than those of clean and uniform samples reported in literature, WWRs offer potential for sugars production.

Keywords Wood waste residues · Acid pretreatment · Enzymatic hydrolysis · Sugars

Introduction

According to the Environmental Protection Agency–EPA [1], the term “urban wood waste” refers to an array of woody materials such as yard trimmings, wood from construction and demolition (C&D) projects, site removals, pallets, furniture, packaging, and other commercial or household wood waste that is otherwise disposed of in landfills [2]. There are three major sources of waste wood in the United States: municipal solid waste (MSW), construction and demolition (C&D) activities, and wood residues from timber-related industries [3]. The EPA estimated that in the US, in 2013, MSW was constituted by 15 Mt of waste wood (6 % of the total MSW generated that year) and C&D debris was constituted by 40.2 Mt of waste wood (8 % of the total C&D debris generated in 2013), from which, 37.7 Mt corresponded to demolition debris [4]. While most of the wood residues from forest products industries have found value-added markets in products such as particleboard, fiberboard, and wood plastic composites, wood wastes residues (WWRs) integrated within MSW stream are often not recovered or have little value due to high non-lignocellulosic materials contamination. However, WWRs in C&D offer some unique attributes that are conducive to recycling. In many urban regions throughout the US, C&D material recycling facilities (MRFs) provide a recovered source of wood that is often sold as hog fuel and in some regions for pulp and paper, along with wood composites if sufficient quality (i.e., reduced amount of contaminates) is achieved [5].

Although C&D WWRs are normally readily available, there are some factors that limit their use. These limitations are related with the lack of “uniformity” (or homogeneity) of properties, compared to “clean” (virgin) wood. Inconsistent physical properties such as density, ash content, and

✉ Manuel Raul Pelaez-Samaniego
m.r.pelaezsamaniego@wsu.edu;
manuel.pelaez@ucuenca.edu.ec

[1] Composite Materials and Engineering Center, Washington State University, Pullman, WA 99164-1806, USA

[2] Present Address: Faculty of Chemical Sciences, Universidad de Cuenca, Av. 12 de Abril, Ciudadela Universitaria, Cuenca, Ecuador

moisture content, plus the presence of contaminates such as metals, resins from wood composites, and paints can potentially hinder transforming WWRs into usable products, including liquid biofuels. Variations in properties and presence of contaminants have largely been recognized as challenging characteristic of these materials for using them through thermochemical operations (e.g., combustion and gasification). Therefore, flexible pretreatment operations able to be adapted for processing materials with different characteristics are required for using WWRs [6]. Currently, WWRs are in part used as fuel for power generation via combustion [7–9], co-firing with other fuels, including coal [10–12], and as a feedstock for paper and wood composites [5, 13]. A number of studies have reported that particleboard and other wood composites, as well as wood chips, compost, and lumber can be produced from WWRs. Wood composites' properties are comparable with those of composites produced with clean/virgin wood [13–15].

The abundance of WWRs has opened doors for investigating their use in different areas such as gasification [6]. An option that could be of interest for using these materials is the production of biofuels, via chemical routes. Nevertheless, further study is necessary to understand the potential or possible limitations of using these materials for producing sugars and liquid biofuels via enzymatic hydrolysis. In the conversion of biomass to a liquid fuel, biomass composition plays a key role in deciding the best strategy for both pretreatment and enzymatic hydrolysis process and the effectiveness of the process [16]. The chemical composition of the biomass plays an intricate role in their feasibility for using it as a feedstock for biofuels via enzymatic hydrolysis. Use of WWRs can be challenging due to the lack of uniformity of the material, which could impact not only the processing operation but also probably increase the amount of inhibitors for fermentation of sugars. The objective of this work was to use WWRs for sugars production via enzymatic hydrolysis and determine possible limitations when this chemical route is employed.

Materials and Methods

Materials

Four samples of wood waste materials derived from construction and demolition debris (approximately 9 kg each) were obtained from three regional MRFs (herein referred to as companies A, B, and C) in the NW United States. The first sample, herein referred to as "A.1", was provided by company A, located in the Seattle (WA) area (names are not provided due to confidentiality). Two more samples, provided by Company B (also located in the Seattle area), have been identified by the company as mulch and hog fuel, and in this work they are referred to as "B.1" and "B.2", respectively. An additional sample, herein referred to as "C.1" was provided by a company located in Portland (OR) area (Company C) and is sold as hog fuel. Figure 1 shows pictures of the four samples. Throughout this paper, all these materials will be referred to as WWRs.

It is known that sampling of heterogeneous materials such as WWRs is not a straightforward process [17, 18]. Therefore, the sampling of the WWRs used in this work relied upon the expertise of the MRFs and was similar to that normally conducted for a typical wood waste stream. MRFs guaranteed us that the samples were randomly selected from the commercial wood waste streams, that no effort was made to clean or separate the materials (i.e., isolate samples for our intent), and that the samples are representative of the materials available at the recycling facilities.

Other materials used in the experimental work included: Sulfuric acid (H_2SO_4, 95–98 % Assay) and acetic acid, both from J.T.Baker; sodium bisulfite ($NaHSO_3$, granular, 58.5–67.4 % assay; Spectrum Chemical Mfg. Corp., NJ). Two types of enzymes, CTec2 and HTec2, used for enzymatic hydrolysis, were complimentary provided by Novozymes North America (Franklinton, NC). Furfural (99 %) and 5-(Hydroxymethyl)furfural (HMF) ($\geq$99 %) purchased from Sigma-Aldrich.

Identification of Wood Species and Preparation of Samples

One of the characteristics of WWRs is that identification of the wood species in samples is very difficult. In our case, since the wood materials came from the NW United States, we expected that the materials will be constituted predominately by Douglas-fir hemlock and other local softwood species that are commonly utilized in the area. In order to confirm this supossition, an estimation of the presence of softwood or hardwood species in the samples was conducted using light microscopy, which helped to visualize the cross section of some wood particles. Thirty particles (approximate dimensions of 20 × 10 × 10 mm) were randomly selected from each sample (i.e., 120 total) and prepared for microscopy, following reported procedures [19, 20]. From the 120 particles, only 3 were identified as hardwood species. Therefore, this work is based on the assumption that the samples are constituted primarily by softwood species and fragments of wood composites produced from softwood species.

Initial inspection of the WWR samples showed that samples A.1 and B.1 contained small amounts of metallic pieces (steel nails and staples) and sample C.1 contained fragments of plastics and fabrics. Samples A.1, B.1, and C.1 showed wood composite particles [e.g., fiberboard, plywood, isolating board, and oriented strand board

A.1 B.1 B.2 C.1

Fig. 1 Pictures of the WWR samples as received (*upper row*) and as used for the SPORL process (*lower row*). The "as received" samples were constituted by mixes of splinters, chips, slivers, wood composites fragments, and other extraneous materials (both metallic and non-metallic), in some cases visible to the naked eye

(OSB)], as well as foam fragments, small rocks, and parts of fabrics. Sample B.2, conversely, was visibly more uniform and cleaner (Fig. 1). After drying at room conditions for 2 weeks, a strong magnet was used to remove ferromagnetic metal contaminants. Plastic and fabric fragments were then removed manually. The amount of metals and plastics/fabrics removed from sample A.1 was negligible (less than 0.1 %, odb). Sample B.1 was constituted by 0.4 % (odb) of ferromagnetic metals. No ferromagnetic metals were detected in sample B.2 but fabrics and plastics and other contaminants constituted approximately 0.6 % (odb) of the weight of this sample. Similar behavior was observed in sample C.1.

Quantification of the presence of wood composites in the materials *as received* was conducted by randomly taking ~500 g of each sample, in triplicate, and manually separating wood composites from wood particles (except for fines). Results showed that the percentages of composites were 16.8 ± 4.3, 4.9 ± 1.3, 34.9 ± 5.4, and 18.2 ± 2.7 % for A.1, B.1, B.2, and C.1, respectively. The composites were put back in the samples immediately after this process. The four samples were subsequently subjected to classification by particle size using a shaker screen apparatus, equipped with two screens: a 25 × 25 mm and a 12.5 × 12.5 mm mesh. Materials used for pretreatment and enzymatic hydrolysis passed through the 25 × 25 mm mesh screen and were retained by the 12.5 × 12.5 mm mesh screen. The decision on using this fraction of materials was based on previous works that used wood chips and/or large wood particles to selectively remove ash and perhaps some non-woody contaminants for SPORL pretreatment [21, 22].

Characterization of the WWRs

Characterization of the raw materials used for pretreatment (i.e., those that passed through the 25 × 25 and were retained by the 12.5 × 12.5 mm mesh screens) included the quantification of ash content, ethanol/toluene extractives content, and carbohydrates content. A representative portion of each material (~500 g) was subjected to a preliminary grinding process, using a granulator knife mill, equipped with a 6.35 mm screen. A randomly removed portion of each resulting material (~60 g) was afterward subjected to a final grinding process using a lab Wiley® mill equipped with a 40 mesh screen.

Ash content was determined following ASTM D1102 [23], using ~2.5 g of oven dried sample, in triplicates. For comparison, ash content was also determined in the materials as received (i.e., in the original material). For this, a representative portion of the material (~0.5 kg) was separated and ground using the same process described above. *Carbohydrates content* in materials used for pretreatment was determined following NREL method [24], using extracted materials. *Extractives* quantification was conducted in one step as per ASTM D1107 [25], using a soxhlet extraction aparatus with ethanol/toluene as solvent. All tests were conducted in duplicates. For carbohydrates content, 150 ± 7 mg of each sample were hydrolyzed with 72 % sulfuric acid in a water bath (30 °C) for 1 h. Then, 42 mL of E-pure water were added and the tubes, after capping, were autoclaved at 121 °C for 1 h. The hydrolysis solution was afterward vacuum filtered using filtering glass crucibles (Corning crucible 30 mL, medium porosity), previously burned at 550 °C for 3 h. An aliquot of the filtrate was used for quantification of acid soluble lignin and sugars content. The soluble lignin was determined using a UV-VIS spectrometer (200–250 wavelength). The sugars composition was studied via ion chromatography (IC) (Dionex ICS-3000 system) (see "Analytical Methods" section). The residues on the crucibles, on the other hand, were dried (105 °C, 24 h), weighed, and then burned in a furnace at 550 °C for 12 h.

Pretreatment

Pretreatment was based on the SPORL (Sulfite Pretreatment to Overcome the Recalcitrance of Lignocelluloses) process [26, 27]. The pretreatment was conducted at referential conditions of 165 °C and 75 min, similar to those previously tested by Zhang et al. [28], using directly (i.e., without grinding) the particles that passed through the 25 mm mesh screen were retained by the 12.5 mm mesh screen. The pretreatment was carried out in a 1-L Parr 4521 bench top reactor controlled by a 4842 Parr controller and coupled with a water circulating cooling system, as described elsewhere [29]. The reactor's internal stirring system was removed for the pretreatment to increase the free volume and hold large particles inside the reactor. The tests were conducted in duplicate, employing 40 g of wood (dry basis) for each run and an amount of acid solution to keep a solution/wood ratio of 3:1. The acid solution (9.8 H_2SO_4 w/w % and 4.6 w/w % $NaHSO_3$, oven dry basis; pH 1.73) was added to the wood previously put in a glass liner inside the Parr reactor. Preliminary tests with the Parr reactor showed that it takes a relatively long time to reach the set temperature (e.g., 46 min to reach 165 °C from room temperature conditions). Since the pre-heating step is long in comparison with the isothermal step, degradation of wood constituents can take place even before reaching the set temperature. In such processes, Borrega et al. [30, 31] suggested adding a time-temperature correction factor (t_T). The activation energy (E_a) of the feedstocks (determined as peer ASTM E1641 [32]), used for computing the t_T, resulted in approximately 180,000 kJ mol^{-1} in all cases. The *degradation rate* required in the equation of Borrega et al. [30, 31] was computed as the ratio of the sample mass reduction during the pretreatment to the isothermal pretreatment time [29]. The results of the t_T were then added to the isothermal process time. It was found that approximately 3 min are necessary to add to the time at isothermal conditions. Therefore, the equivalent isothermal process was 78 min instead of 75 min. The isothermal pretreatment temperature, on the other hand, fluctuated in the range 165 ± 3 °C during the test due to difficulty to keep constant the isothermal temperature in the Parr reactor. After the pretreatment, part (approximately 40 ml) of the prehydrolysate (pretreatment liquor) was collected and used for sugars content analyses using Ion Chromatography. The solid materials, conversely, were immediately washed with tap water for at least five times.

Enzymatic Hydrolysis

Enzymatic hydrolysis was conducted following previous works [26, 27] with a minor modification: the pretreated materials were ground using a lab Wiley® mill with a 40-mesh screen (instead of disc milling, as in the case of the referred works), due to the difficulty of using a disk mill for small amounts of materials. The washed pretreated solids were dried for 12 h at approximately 60 °C to help the grinding process prior enzymatic hydrolysis. The enzymatic hydrolysis process was performed using 7.5 g (odb) of pretreated material (passed through the 40 mesh screen) at 10 % (w/w) solids concentration in 250 mL flasks, using a 50 mM buffer acetate, adjusted to pH 5 with sodium acetate, which was close to pH 5.5, used in previous works [27, 28]. The enzyme loadings were 5 % w/w (dry pretreated wood basis) of CTec2 and 0.5 % w/w (dry pretreated wood basis) of HTec2. The density of the enzymes was 1.2 g mL^{-1}. After sealing with aluminum foil, the flasks (in duplicates) were put in an incubator shaker. The conditions of the process were 50 °C and 200 rpm, for 72 h. After hydrolysis, an aliquot of each hydrolysate was collected in centrifuging tubes and, after sealing, heated at 95 °C for 10 min using a dry bath (AccuBlock, Labnet Inernational, Inc.) for enzyme deactivation. The products were then centrifuged (accuSpin Micro

Table 1 Ash content and ethanol/toluene extractives of the samples used for the pretreatment (odb mass%)

Sample	Ash (%) materials "as received"	Ash (%) materials for pretreatment	Extractives content (%)
A.1	1.21 ± 0.10	1.16	4.22
B.1	0.83 ± 0.14	0.64	3.79
B.2	10.08 ± 1.69	3.39	3.12
C.1	2.01 ± 0.18	2.53	3.50

The second column shows the ash content of the material "as received" for comparison

Table 2 Carbohydrates composition (in dry and extractives removed basis) of WWR samples

Polymeric sugar/lignin	A.1 (%)	B.1 (%)	B.2 (%)	C.1 (%)
Arabinan	1.14	1.27	1.10	0.94
Galactan	2.57	2.63	1.87	2.01
Glucan	39.67	41.15	41.28	44.12
Xylan/mannan	14.29	15.47	14.35	15.26
Total carbohydrates	57.66	60.52	58.59	62.33
Lignin	36.18	34.82	33.34	32.42

Table 3 Pretreated biomass yields and pH of prehydrolysates

	A.1 (%)	B.1 (%)	B.2 (%)	C.1 (%)
Yield	75.42	78.68	77.8	78.35
pH	1.41	1.54	1.55	1.51

17, Fisher Scientific) and the supernatant collected for sugars analysis.

Analytical Methods

The carbohydrates content of the solid fraction after the pretreatment process was determined similarly than in the case of the feedstock ("Characterization of the WWRs" section). The prehydrolysate (pretreatment liquor), conversely, was tested for sugar oligomers content by means of Ion Chromatography (IC), using a Dionex ICS-300DC, coupled with Dionex AS auto sampler, and ICS-3000SP and ICS-3000EO modules. For the test, the liquid was filtered using 0.2 μm microfilters. The filtered liquid was then dissolved with E-pure water prior analysis. Similar test was conducted to quantify the sugars content in the hydrolysate.

The presence of furan compounds (expected to be fermentation inhibitors) in the pretreatment liquor was determined using high performance liquid chromatography (HPLC). The equipment was a VARIAN Prostar 230 HPLC, coupled with a 350 RI detector and a Prostar 410 autosampler. The test was conducted using a HPX-87H Bio-Rad Aminex column (300 × 7.8 mm), which operated in a Timberline 101 oven at 85 °C. The flow rate was 0.6 ml min^{-1}. Calibration of the equipment was conducted using acetic acid, furfural, and 5-(Hydroxymethyl)furfural (described in "Materials" section).

Results and Discussion

The moisture content of the samples *as received* was 12.78 ± 0.73, 14.30 ± 0.34, 25.21 ± 0.46, and 8.55 ± 0.45 % for A.1, B.1, B.2, and C.1, respectively. After drying at room conditions the MC was reduced to 5.42 ± 0.29, 5.99 ± 0.1, 6.09 ± 0.03, and 5.90 ± 0.08 %, for A.1, B.1, B.2, and C.1, respectively. Particle size distribution analyses of the WWR samples showed that the fractions that passed through the 25 × 25 mm and were retained by the 12.5 × 12.5 mm constituted 39 ± 3, 52 ± 4, 48 ± 4, and 45 ± 3 % of the original sample for A.1, B.1, B.2, and C.1, respectively.

Ash and Extractives Content

The ash content of the materials used for the pretreatment and in the samples *as received* is presented in Table 1. Ash content remains approximately equal after separating the sample for pretreatment, except in the case of B.2, in which a threefold reduction of ash content is observed, suggesting that classification of materials by particle size before pretreatment could be a strategy to reduce ash content in this sample. The extractives content, also shown in Table 1, shows that there are no important differences in the amount of ethanol/toluene extractives among the samples.

Carbohydrates Content

The total carbohydrate content of the WWR samples (Table 2) ranges from approximately 58–63 %. These results are comparable to values of other types of wood materials, such as Loblolly pine and FS-10 Douglas-fir forest residues (i.e., 51.8 and 59.4 %, respectively, as shown in other works [27, 33]), but relatively lower than those of Douglas-fir chips (obtained from a pulp mill) (i.e., 64 %) [27]. Lignin content of WWRs is, on the other hand, higher than in FS-10 (i.e., 29.3 %, as reported by Zhu et al. [27].

Results of the Pretreatment Process

The yields of the pretreatment process and the pH values of the prehydrolysates (i.e., pretreatment liquor) is presented in Table 3. The results show that the pretreatment process

Table 4 Carbohydrates and lignin composition (dry basis) of the pretreated materials

Polymer sugars	A.1 (%)	B.1 (%)	B.2 (%)	C.1 (%)
Arabinan	0.80 (38.5)[b]	0.00	0.00	0.00
Galactan	1.40 (29.7)	0.44 (9.8)	1.23 (38.1)	1.22 (35.9)
Glucan	66.66 (91.5)	58.80 (85.1)	58.53 (82.3)	58.47 (78.5)
Xylan/mannan	7.28 (27.8)	6.67 (25.7)	8.82 (35.7)	8.29 (32.2)
Total carbohydrates	76.1	65.9	68.6	68.0
Total carbohydrates recovery (%)[a]	95.4	82.4	87.3	82.5
Lignin	28.1	27.8	25.4	27.3

[a] Refers to the ratio, in percent, of the carbohydrates in pretreated materials to the carbohydrates in the corresponding feedstocks

[b] The value in parenthesis refers to the percentage recovery of the corresponding sugar

Table 5 Prehysdrolysate composition (% of the corresponding carbohydrate in the feedstock)

Sugar	A.1 (%)	B.1 (%)	B.2 (%)	C.1 (%)
Arabinose	1.1	1.9	1.8	1.1
Galactose	19.2	7.0	9.0	19.6
Glucose	3.0	1.0	1.2	2.1
Xylose/mannose	13.6	11.6	14.0	10.3
% Recovery in prehydrolysate	6.29	5.33	6.11	6.21
Furfural (g L^{-1})	3.67	5.36	3.30	4.31
HMF (g L^{-1})	5.05	7.25	1.74	10.90
Total furan (g L^{-1})	16.10	20.91	13.43	24.16
Acetic acid (g L^{-1})	7.38	8.30	8.40	8.95

Table 6 Total sugar yields (in monomeric sugars base)

	A.1 (%)	B.1 (%)	B.2 (%)	C.1 (%)
Sugars in prehydrolysate	6.29	5.33	6.11	6.21
Sugars in enzymatic hydrolysate	49.43	60.28	53.84	52.25
Total recovery (%)	55.72	65.61	59.95	58.46

provides high yields of solids, which are close to those obtained in other works involving mild bisulfite pretreatment of softwood species (i.e., 74.9 % for lobolly pine chips (with bark) and 69.3 % for debarked maple chips) [33]. The carbohydrates composition of the pretreated WWRs is presented in Table 4, which also presents the total carbohydrate recovery and shows that the carbohydrate recovery varies depending on the feedstock. Samples A.1 and C.1 show the highest recoveries (95.4 and 87.3 %, respectively). Component recoveries, shown in parentheses in Table 4, indicate that glucan recovery is, as expected, the highest among sugars but that it also varies depending on the WWR source.

The composition of the prehydrolysate is presented in Table 5. In addition to the sugars produced from the hydrolysis process, Table 5 shows the percentages of furans. The total furans content (i.e., 16.1, 20.9, 13.4, and 24.2 g L^{-1} for A.1, B.1, B.2, and C.1, respectively) are higher (approximately double) than in other works. For instance, Zhang et al. [28] reported total furans content of 7.39 g L^{-1} (i.e., 1.35 g $^{-}L^{-1}$ for HMF, 2.02 g L^{-1} for furfural, and 4.02 g $^{-}L^{-1}$ for acetic acid), using the same pretreatment process and similar conditions, but with a different feedstock (FS-10). One of the possible reasons for higher furan contents in pretreated WWRs is the presence of wood composites and the inherent adhesives and additives present in wood composites. As mentioned above, the presence of wood composites in WWR samples can be as high as 35 %. Thus, any change to the structure and composition of wood used for composites, as a consequence of heating, could affect the pretreatment process.

Enzymatic Hydrolysis and Total Sugar Yields

The sugars content in the hydrolysates is presented in Table 6. The total sugar yield of the whole process is

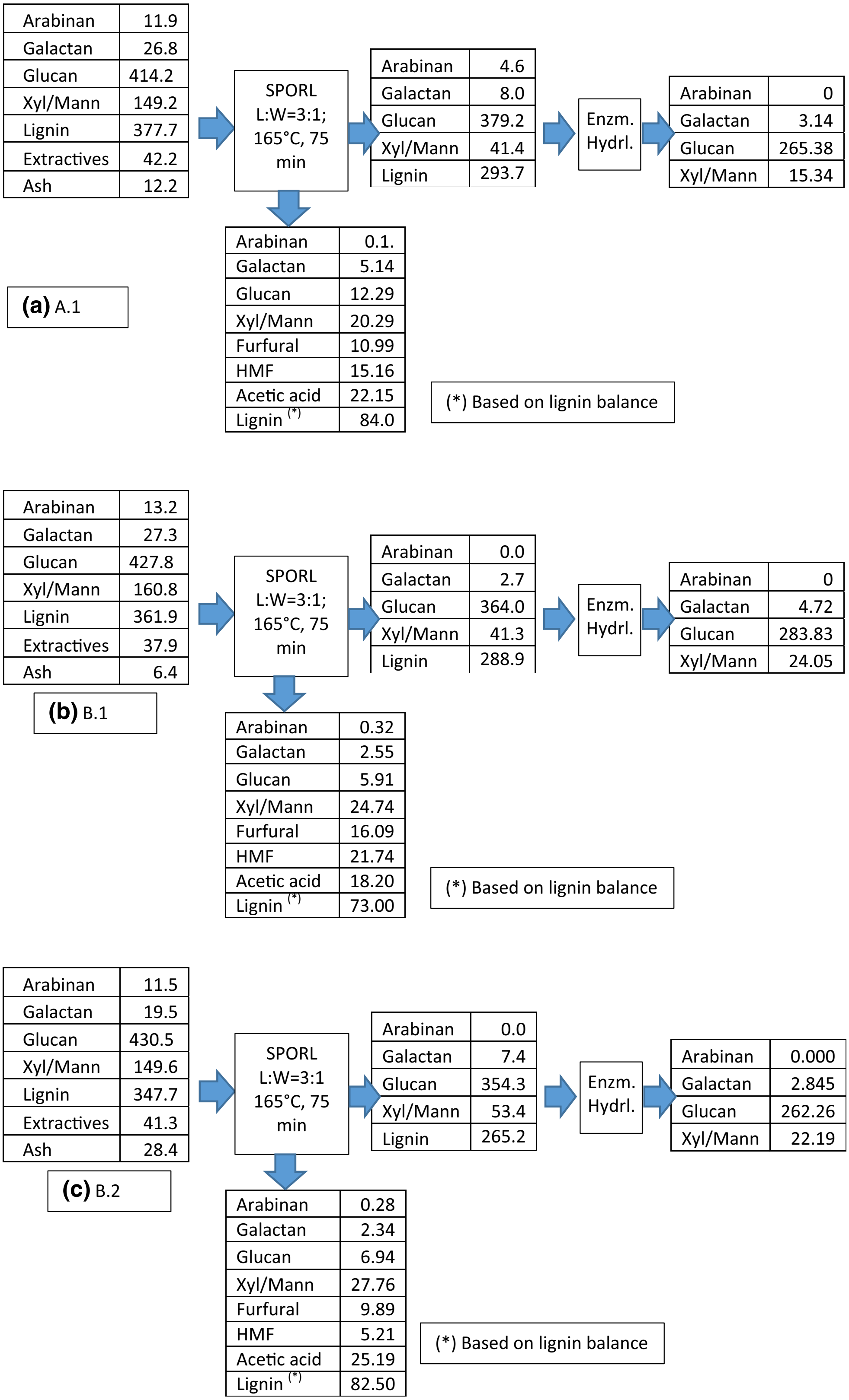


Fig. 2 **a** Overall mass balance for acid pretreatment and enzymatic hydrolysis of waste wood residues, based on 1000 g (or kg) of sample of: **a** A1, **b** B2, **c** B3, and **d** C4

(a) A.1

Arabinan	11.9
Galactan	26.8
Glucan	414.2
Xyl/Mann	149.2
Lignin	377.7
Extractives	42.2
Ash	12.2

SPORL L:W=3:1; 165°C, 75 min

Arabinan	4.6
Galactan	8.0
Glucan	379.2
Xyl/Mann	41.4
Lignin	293.7

Enzm. Hydrl.

Arabinan	0
Galactan	3.14
Glucan	265.38
Xyl/Mann	15.34

Arabinan	0.1.
Galactan	5.14
Glucan	12.29
Xyl/Mann	20.29
Furfural	10.99
HMF	15.16
Acetic acid	22.15
Lignin (*)	84.0

(*) Based on lignin balance

(b) B.1

Arabinan	13.2
Galactan	27.3
Glucan	427.8
Xyl/Mann	160.8
Lignin	361.9
Extractives	37.9
Ash	6.4

SPORL L:W=3:1; 165°C, 75 min

Arabinan	0.0
Galactan	2.7
Glucan	364.0
Xyl/Mann	41.3
Lignin	288.9

Enzm. Hydrl.

Arabinan	0
Galactan	4.72
Glucan	283.83
Xyl/Mann	24.05

Arabinan	0.32
Galactan	2.55
Glucan	5.91
Xyl/Mann	24.74
Furfural	16.09
HMF	21.74
Acetic acid	18.20
Lignin (*)	73.00

(*) Based on lignin balance

(c) B.2

Arabinan	11.5
Galactan	19.5
Glucan	430.5
Xyl/Mann	149.6
Lignin	347.7
Extractives	41.3
Ash	28.4

SPORL L:W=3:1 165°C, 75 min

Arabinan	0.0
Galactan	7.4
Glucan	354.3
Xyl/Mann	53.4
Lignin	265.2

Enzm. Hydrl.

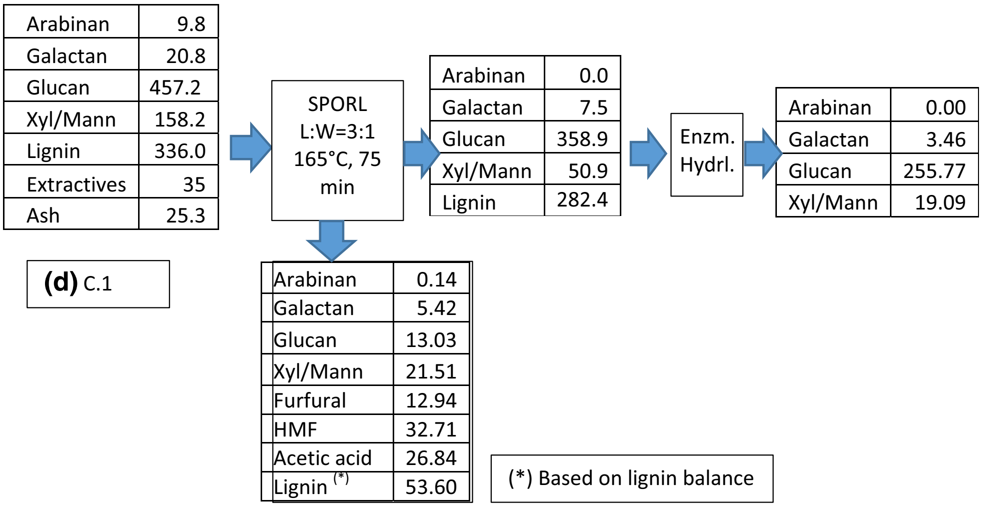
Arabinan	0.000
Galactan	2.845
Glucan	262.26
Xyl/Mann	22.19

Arabinan	0.28
Galactan	2.34
Glucan	6.94
Xyl/Mann	27.76
Furfural	9.89
HMF	5.21
Acetic acid	25.19
Lignin (*)	82.50

(*) Based on lignin balance

presented as the sum of the sugars percent in the prehydrolysate and the sugars content in the hydrolysate. The yields are, in general, relatively lower than values reported in the literature for other types of wood samples, either using similar or different types of enzymes for the enzymatic hydrolysis process. For example, Gao et al. [33] used

Fig. 2 continued



similar temperature and time conditions for pretreatment but different sulfonation conditions and different wood samples. In the referred work, the yields of sugars were 85.8 % for softwood un-debarked loblolly pine and 94 % for debarked sugar maple chips. Likewise, Zhang et al. [28], using similar pretreatment conditions and Douglas fir obtained approximately 75 % of sugars yield. In both cases, the yields are higher to those presented in Table 6. Sample B.1 shows the highest sugars recovery (due to the lower amount of wood composites), A.1 presents the lowest sugars recovery, and that B.2 and C.1 show approximately similar sugars recovery. Lower yields could be in part explained by the presence of wood composites in WWR samples.

Wood composites are normally produced via hot pressing, at temperatures close to or above 160 °C. It is expected that some modification of wood constituents happens during the pressing process. Several works have demonstrated that, at these conditions, lignin is depolymerized and hemicelluloses are partially degraded. Lignin is also subjected to some degree of plasticization and partial migration from the wood cell walls to the surface of the wood fibers. Lignin in these conditions is able to adhere to cellulosic fibers and partially cover the fibers with a lignin-rich layer [19, 29, 34, 35]. Although this lignin "layer" has a positive effect for protecting wood (i.e., wood composites) from moisture [35], it could adversely impact the enzymes activity during enzymatic hydrolysis [36]. Research has also showed that at relatively low temperatures (e.g., close to 300 °C), cellulose is subjected to cross linking [37]. Although there is no evidence that crosslinking of cellulose happens at temperatures similar to those employed for wood composites pressing, Lowary and Richards [38] showed that at 171 °C (in which expected reactions do not involve mass loss), cellobiitol (a disaccharide surrogate, used as a model of cellulose) undergoes intermolecular nucleophilic substitution at the hydroxyl groups, which was responsible for the production of large oligosugars. These observations suggest that the hot pressing for composites manufacture could have altered the composition and structure of wood, which could consequently explain, at least in part, the lower yields of sugars produced via enzymatic hydrolysis using WWRs. This could also explain why B2, which contains less wood composites than the other samples, yielded higher sugars recovery. Other reasons for lower yields (compared to yields reported in literature) could be: (a) the type of reactor (in this work we used a small Parr reactor, without agitation, instead of a large one, as in the work of Cheng et al. [22]), and (b) the type of particles we used in this work for enzymatic hydrolysis (i.e., wood flour instead of fibers).

Process Mass Balance

General mass balances of the whole process (i.e., pretreatment plus enzymatic hydrolysis) for each WWR, is presented in Fig. 2a–d. The mass balances are based on 1000 g of sample in all cases. In the figures, the down arrow represents the residues from the SPORL treatment. The balances are relatively similar, except for B.1 sample, which shows higher potential as a raw material for production of sugars via enzymatic hydrolysis due to three important reasons: (a) the yield of sugars is higher than in the case of the other feedstocks, (b) the ash content is lower than in the other materials, and (c) the amount of composites in this material is lower than in the other feedstocks.

Conclusion

Samples of construction and demolition wood waste residues (WWRs) from three different suppliers in the NW United States were used for production of sugars using the

SPORL pretreatment, followed by enzymatic hydrolysis. This work shows that it is feasible to produce sugars from WWRs. The pretreatment process allowed recovery in the range from 75 to 79 % (mass basis). Carbohydrates in pretreated materials varied from 66 to 76 % (mass basis). Results of the enzymatic hydrolysis indicate that the sugar yields (varying from 49 to 60 %) depend on the material source. In general, results suggest that the cleaner the sample, the higher the yield of sugars. Moreover, the presence of wood composites appears to affect the total sugars yields. The total sugars yields varied from 56 to 66 %. Although the total yields are relatively lower than those of other (clean and uniform) samples reported in literature, from a technical point of view, WWRs offer potential for sugars production.

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