energy&fuels

Article

pubs.acs.org/EF

Chemical Composition and Biofuel Potentials of a Wide Diversity of Plant Biomasses

Bruno Godin,*[,†,‡] Stéphane Lamaudière,[‡] Richard Agneessens,[†] Thomas Schmit,[†] Jean-Pierre Goffart,[†] Didier Stilmant,[†] Patrick A. Gerin,[‡] and Jérôme Delcarte[†]

[†]Biomass, Bioproducts and Energy Unit, Valorisation of Agricultural Products Department, Walloon Agricultural Research Center (CRA-W), Chaussée de Namur, 146, B-5030 Gembloux, Belgium

[‡]Bioengineering Group, Earth and Life Institute, Université catholique de Louvain, Croix du Sud, 2 box L7.05.19, B-1348 Louvain-la-Neuve, Belgium

Supporting Information

ABSTRACT: The chemical composition of 1052 samples covering 49 plant species is summarized in this paper. The analyzed biomasses offer a wide range of chemical compositions, monosaccharidic compositions of hemicelluloses, enzymatically digestible organic matter, and bioethanol potential. Nevertheless, their thermal energy value remains in a narrow range on a dry matter basis. Biomasses that were identified as best suited for anaerobic digestion are characterized by low contents of cellulose, hemicelluloses, and lignin and high contents of non-structural constituents. Biomasses most suited for combustion present the lowest content of mineral compounds, and the most adequate biomasses for bioethanol conversion have high contents of total carbohydrates. Interestingly, the observed chemical compositions tend to cluster the biomasses in composition groups that also correspond to phylogenetic groups: commelinids, non-commelinid magnoliophyta, and pinophyta species. Some groups can clearly be subdivided into fibrous and moderately fibrous biomasses.

1. INTRODUCTION

To reduce simultaneously human-induced global warming and the depletion of fossil fuel resources, alternative energy production chains are necessary.[1] Plant biomasses are one of the promising sources of renewable and sustainable energy.[2,3] Cellulose (linear homogeneous structural polysaccharide composed of D-glucose units), hemicelluloses (ramified heterogeneous structural polysaccharides composed of D-xylose, L-arabinose, D-mannose, D-galactose, and D-glucose units), lignin (phenyl propanoid polymer composed of syringyl, guaiacyl, and *p*-hydroxyphenyl units), pectins (ramified heterogeneous structural polysaccharides mainly composed of D-galacturonic acid units), soluble sugars (D-glucose, D-fructose, sucrose, and fructans), starch (linear or ramified homogeneous non-structural polysaccharide mainly composed of D-glucose), proteins, and mineral compounds are the main chemical components of plant biomasses.[4,5] These components (except mineral compounds) and lipids represent the pool of organic carbon coming from the photosynthetically collected and stored solar energy.[6] They represent a huge amount of renewable resource for a sustainable bio-based economy. The optimal valorization of these biomass components, for green chemistry and/or for biofuel production, requires a good knowledge of the contents and molecular composition of their components.[2,7] The chemical composition depends upon the plant species.[3,5,8] The contents of structural components depend upon the degree of lignification of the cell wall. Stems are richer in secondary cell walls (which have a high cellulose content) and highly lignified primary cell walls, as compared to leaves.[4] In the case of hemicelluloses, the content of their monosaccharidic components (D-xylose, L-arabinose, D-mannose, D-galactose, and D-glucose) depends upon the phylogenetic origins of the plant species. The hemicelluloses of commelinid biomasses have higher contents of xylan and arabinan, associated as arabinoxylan, and *β*-glucan.[4] The hemicelluloses of non-commelinid magnoliophyta biomasses have higher contents of hemicellulosic glucan, in the form of xyloglucan, and mannan.[4] The hemicelluloses of pinophyta biomasses have a higher content of mannan.[4] Primary cell walls have higher contents of xyloglucan, *β*-glucan, and mannan, as compared to secondary cell walls that have a higher content of arabinoxylan.[4,9,10]

Whole plant biomasses can be used to produce bioenergy (thermal, electrical, and mechanical energy) by converting their chemical components into biofuel (solid, liquid, or gaseous).[3] Dependent upon its composition, each type of biomass can be better suited to specific types of conversion processes. To rapidly compare the energy value of biomasses and their suitability for conversion processes, we selected three properties, in addition to the chemical composition: (1) the higher heating value (HHV; MJ kg^{-1}_{DM}), as an assessment for conversion by combustion;[2,3] (2) the bioethanol potential, calculated following the methodology by Spatari et al.;[11] and (3) the enzymatic digestibility (nutritional value), following the methodology by De Boever et al.,[12,13] as a fast assessment of the anaerobic digestibility (biomethanation) without any pretreatment of the biomass.

The present study investigated a wide diversity of plant biomasses to determine their chemical composition (cellulose, hemicelluloses, lignin, total soluble sugars, starch, proteins, and

Received: November 26, 2012
Revised: March 14, 2013
Published: March 18, 2013

dx.doi.org/10.1021/ef3019244 | Energy Fuels 2013, 27, 2588−2598

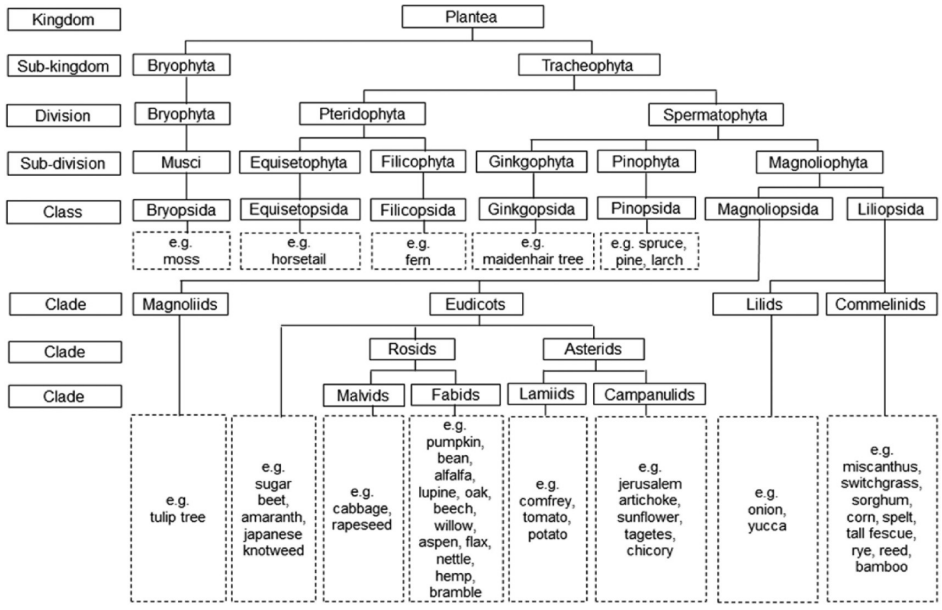

Figure 1. Phylogenetic origins of the analyzed biomasses.

mineral compounds), the monosaccharidic composition of their hemicelluloses (xylan, arabinan, mannan, galactan, and hemicellulosic glucan), their content of enzymatically digestible organic matter (DOM), and their bioethanol and thermal energy potential. The possibility to classify and cluster the biomass types depending upon their chemical composition was tested, as well as the correlation between biomass chemical composition and the corresponding enzymatically DOM, bioethanol, and thermal energy potential. Lipids were considered as a negligible component in the type of biomasses investigated in the present study and were not analyzed.

2. MATERIALS AND METHODS

2.1. Biomass Material. The collected samples included miscanthus giganteus (*Miscanthus x giganteus* J.M. Greef & Deuter ex Hodk. & Renvoize; cultivars: Bical and Tournai; early autumn and late winter harvest, respectively, 21 and 74 samples), switchgrass (*Panicum virgatum* L.; cultivars: Alamo, Blackwell, Cave-in-Rock, Dacotah, Kanlow, Nebraska 28, Shelter, and Traiblazer; early autumn and late winter harvest, respectively, 22 and 128 samples), fiber sorghum [*Sorghum bicolor* (L.) Moench; cultivars: CA25, ENR10, H133, Maja, and Zerberus; early autumn and late winter harvest, respectively, 92 and 53 samples], spelt straw [*Triticum aestivum* L. ssp. *spelta* (L.) Thell.; cultivars: Badengold and Cosmos; late summer harvest; 79 samples], "cocksfoot−alfalfa" mixture (*Dactylis glomerata* L. cultivar Terrano−*Medicago sativa* L. cultivar Europe; 3 harvest cycles late spring−late summer−late autumn; 27 samples), tall fescue (*Festuca arundinacea* Schreb.; cultivars: Hykor, Jordane, Kora, Perun, and Soni; 3 harvest cycles late spring−late summer−late autumn; 175 samples), immature rye (*Secale cereale* L.; cultivars: Protector and Vitalio; early spring harvest; 54 samples), fiber corn (*Zea mays* L.; cultivars: Aayrton, Athlético, Aventura, Beethoven, Cannavaro, Coryphée, Dominator, Franky, Ladifférence, LG Azelo, Olympus, Ricardinio, and Ronaldinio; early autumn and late winter harvest, respectively, 125 and 21 samples), hemp (*Cannabis sativa* L.; cultivars: Epsilon 68, Fedora 17, and Futura 75; early autumn harvest; 80 samples), and Jerusalem artichoke (*Helianthus tuberosus* L.; cultivar: Volkenroder spindel; leaf and stalk; early autumn harvest; 46 samples). These biomasses came from randomized block-designed crop trials performed in 2007, 2008, 2009, and/or 2010 at Libramont [498 m above sea level (asl); average annual temperature, 8.6 °C; average annual precipitation, 1260 mm; 49° 55′ N, 05° 24′ E; Belgium], Gembloux (161 m asl; average annual temperature, 9.8 °C; average annual precipitation, 856 mm; 50° 33′ N, 04° 43′ E), Tinlot (255 m asl; average annual temperature, 8.7 °C; average annual precipitation, 871 mm; 50° 28′ N, 05° 23′ E; Belgium), Mötsch (330 m asl; average annual temperature, 8.4 °C; average annual precipitation, 675 mm; 49° 57′ N, 06° 33′ E; Germany), or Gerbéviller (260 m asl; average annual temperature, 9.9 °C; average annual precipitation, 1022 mm; 48° 29′ N, 06° 31′ E; France). A plot between 9 and 24 m^2 of the whole above ground biomass was harvested for each biomass sample. It was cut at 10 cm from the ground and chopped with a Haldrup M-65 harvester.

The collected samples also included reed [*Phragmites australis* (Cav.) Trin. ex Steud; cultivar: Humilis; late winter harvest; 1 sample], bamboo (*Phyllostachis vivax* Siebold & Zucc; late winter harvest; 1 sample), leaf and bulb of onion (*Allium cepa* L. cultivar: Sonia; early autumn harvest; 1 sample), yucca leaf (*Yucca gloriosa* L.; cultivar: Variegata; late summer harvest; 1 sample), tulip tree wood (*Liriodendron tulipifera* L.; 1 sample), sugar beet leaf and stalk (*Beta vulgaris* L.; cultivar: Angelica, Bernadetta, Mangelan, and Rubens; autumn harvest; 5 samples), amaranth leaf and stalk (*Amaranthus viridis* L.; cultivar: Amar; autumn harvest; 1 sample), Japanese knotweed [*Fallopia japonica* (Houtt.) Ronse Decr.; early autumn harvest; 1 sample], cabbage leaf (*Brassica oleracea* L.; cultivar: Botrytis; early autumn harvest; 1 sample), rapeseed straw (*Brassica napus* L.; cultivar: Aurum; late summer harvest; 1 sample), pumpkin leaf and stalk (*Cucurbita maxima* Duchesne; cultivar: Tromba; early autumn harvest; 1 sample), bean leaf and stalk (*Phaseolus vulgaris* L.; cultivar: Goliath; early autumn harvest; 2 samples), alfalfa leaf and stalk (*Medicago sativa* L.; cultivar: Astra; late spring harvest; 1 sample), lupine leaf and stalk (*Lupinus albus* L.; cultivar: Fortuna; late summer harvest; 1 sample), flax straw (*Linum usitatissimum* L.; cultivar: Linus; late summer harvest; 1 sample), nettle (*Urtica dioica* L.; early autumn harvest; 1 sample), bramble leaf and stalk (*Rubus fruticosus* L.; late summer harvest; 1 sample), comfrey leaf and stalk (*Symphytum officinale* L.; cultivar: De russi; late spring harvest; 2 samples), tomato leaf and stalk (*Solanum lycopersicum* L.; cultivar: Campbell 33; late summer harvest; 4 samples), potato leaf and stalk (*Solanum tuberosum* L.; cultivar: Desiree, Kenebec, and Nicolas; late summer harvest; 1 sample), Jerusalem artichoke tuber (*H. tuberosus* L.; cultivar: Volkenroder spindel; autumn harvest; 2 samples), sunflower leaf and stalk (*Helianthus annuus* L.; cultivar: Giant Russian; early autumn harvest; 2 samples), tagetes (*Tagetes patula* L.; cultivar: Nugget; early autumn harvest; 1 sample), green (autumn harvest; 1 sample) and white (1 sample) leaf of chicory (*Cichorium intybus* L.), unforced (autumn harvest; 2 samples) and forced (2 samples) root of chicory

dx.doi.org/10.1021/ef3019244 | *Energy Fuels* 2013, 27, 2588−2598

(*C. intybus* L.), oak wood (*Quercus* sp.; 1 sample), beech wood (*Fagus sylvatica* L.), willow wood (*Salix* sp.; late winter harvest; 3 years old; 4 samples), aspen wood (*Populus* sp.; 1 sample), spruce wood [*Picea abies* (L.) Karst.; 1 sample], pine wood (*Pinus* sp.; 1 sample), larch wood (*Larix decidua* Mill.; 1 sample), maidenhair tree wood (*Ginkgo biloba* L.; 1 sample), fern [*Pteridium aquilinum* (L.) Kuhn; late spring harvest; 1 sample], horsetail (*Equisetum* sp.; late spring harvest; 1 sample), and moss (*Bryum* sp.; late spring harvest; 1 sample). The biomasses were harvested manually in 2010 and/or 2011 in Wallonia (Belgium).

The phylogenetic origins[14] of the analyzed biomasses are shown in Figure 1.

Immediately after the harvest, two representative subsamples of 750 g of each biomass were directly dried at 60 °C for 72 h in a Memmert UFP800 oven (VWR, Heverlee, Belgium). After drying, the two subsamples were first milled with a 4 mm screen hammer mill (BOA, Waterleau, Herent, Belgium), followed by a second milling step with a 1 mm screen cyclone mill (Cyclotec, FOSS Benelux N.V., Bruxelles, Belgium). The two subsamples were merged and stored in airtight bags at room temperature and protected from light in a dark box.

2.2. Chemical Analyses. All chemicals were of analytical grade or equivalent and were purchased from VWR (Heverlee, Belgium) and Chem-Lab (Zeldelgem, Belgium). Technical duplicate aliquots were measured for each sample, and results were expressed in kilograms per kilogram of DM (103 °C dried matter).

2.2.1. Cellulose, Hemicelluloses, and Monosaccharidic Composition of Hemicelluloses. The cellulose, xylan, arabinan, mannan, galactan, and hemicellulosic glucan contents were determined by liquid chromatography (LC) after fractionation and sulfuric acid hydrolysis (SAH).[15] Briefly, the samples were fractionated by Van Soest (VS) neutral detergent extractions, with extraction 1 being 0.1 mM phosphate buffer at pH 7 for 15 min at 90 °C and extraction 2 being VS neutral detergent for 1 h at 100 °C. For starch-containing samples, 1000 units/$g_{DM\ sample}$ of an analytical thermostable α-amylase (Megazyme, Ireland) was added in the first extraction solution. The xylan, arabinan, galactan, mannan, and total glucan contents of the insoluble residue left after these extractions were determined by a two-stage SAH method, with stage 1 being solubilization by 12.2 mol L^{-1} H_2SO_4 for 1 h at 30 °C and stage 2 being hydrolysis by 0.42 mol L^{-1} H_2SO_4 for 2 h at 121 °C. The released monosaccharides were separated and quantified by a LC system with a Carbo Sep CHO-682 Pb analytical LC column (300 × 7.8 mm inner diameter; 7 μm particle size; Interchrom, Montluçon, France) at 80 °C using deionized water at 0.4 mL/min as the mobile phase and equipped with a charged aerosol detector (CAD). The hemicellulosic glucan content was determined by the SAH method, except that the cellulose solubilization step (incubation with 12.2 mol L^{-1} H_2SO_4 at 30 °C for 1 h) was omitted. The cellulose (cellulosic glucan, i.e., D-glucose of cellulose under its polymeric form) content of the SAH method was calculated as the difference between the total glucan and the hemicellulosic glucan contents. The hemicelluloses content of the SAH method was calculated as the sum of the xylan, arabinan, galactan, mannan, and hemicellulosic glucan contents. The monosaccharidic components (D-xylose, L-arabinose, D-mannose, D-galactose, and D-glucose) of hemicelluloses were expressed under their polymeric form (xylan, arabinan, mannan, galactan, and hemicellulosic glucan).

2.2.2. Lignin. The acid detergent lignin (ADL, weight of the acid detergent fiber residue corrected of its content of mineral compounds) was determined by the VS gravimetric method.[16] Briefly, biomass samples were first extracted with the VS neutral detergent method, as described above, then with VS acid detergent for 1 h at 100 °C, and finally, with 12.2 mol L^{-1} H_2SO_4 for 1−3 h at room temperature.

2.2.3. Total Soluble Sugars. The total soluble sugars were determined by the Luff−Schoorl method.[17] Briefly, the total soluble sugars were first extracted with deionized water for 1 h at room temperature. The extracted solution was clarified with Carrez solutions I and II. The clarified solution was incubated with 0.1 mol L^{-1} HCl for 30 min at 100 °C to invert all sugar. The solution was neutralized with 0.1 mol L^{-1} NaOH to determine the total sugar content by the colorimetric titration of Luff−Schoorl.

2.2.4. Starch. The starch content was determined by the Ewers method.[17] Briefly, this method is made of two parallel analyses. In the first analysis, the sample was incubated with 0.31 mol L^{-1} HCl for 15 min at 100 °C. After clarification of the extracted solution with Carrez solutions I and II, the optical rotation of the solution is measured by polarimetry. In the second analysis, the sample was incubated with 40% (volume percentage) ethanol for 1 h at room temperature. After acidification of the extracted solution with HCl and clarification of it with Carrez solutions I and II, the optical rotation of the solution was measured as in the first analysis. The difference between the two measurements, divided by the specific optical rotation (+184.0°) of starch of vegetal biomasses, gives the starch content of the sample.

2.2.5. Proteins. The protein content was determined by the Kjeldahl method using 6.25 as the conversion factor of nitrogen to protein.[18] Briefly, the sample was mineralized by concentrated H_2SO_4 in the presence of a catalyst (containing K_2SO_4 and $CuSO_4{\cdot}5H_2O$). After mineralization, the acid solution was made alkaline with NaOH. The liberated ammonia was distilled and collected into an excess of H_3BO_3 solution. This solution was then titrated with a HCl solution.

2.2.6. Mineral Compounds. The content of mineral compounds was determined gravimetrically after organic matter oxidation in a muffle furnace set at 550 °C for 3 h.

2.2.7. Soluble Carbohydrate Composition. Soluble carbohydrates were extracted by mixing 500 mg of dried sample with 9.5 mL of deionized water in 15 mL polypropylene tubes. The obtained slurry was incubated at 70 °C for 20 min by immersing the tubes in a water bath, with manually mixing the samples every 5 min. The slurry was centrifuged (2700*g* for 10 min), and the supernatant was collected with a 5 mL syringe and was filtered through a 0.2 μm cellulose acetate filter unit (Sartorius Biolab Products, Vilvoorde, Belgium). The clear filtrate was analyzed by LC using an Agilent 1200 series LC system with a quaternary pump (Agilent, Berkshire, U.K.) connected to a 1200 series Agilent evaporative light scattering detector (ELSD) (Agilent, Berkshire, U.K.). Nitrogen (0.35 MPa) was used as the nebulizer gas. The nebulizer tube temperature was set to 50 °C, and the ELSD gain was set to 9. Sample extracts diluted (from a 1:20 volume fraction to a 1:100 volume fraction) in deionized water with 10% (volume percentage) LC-grade acetonitrile were injected (20 μL) and eluted in a Prevail Carbohydrates ES analytical LC column (250 × 4.6 mm inner diameter; 5 μm particle size; Grace, Lokeren, Belgium) with a Prevail Carbohydrates ES All-guard precolumn (12.5 × 4.6 mm inner diameter; 5 μm particle size; Grace, Lokeren, Belgium). The mobile phases consisted of (A) 95:5 (volume fraction) LC-grade acetonitrile/deionized water mixture and (B) 100% deionized water. The gradient condition was 0−15 min, 20−50% volume percentage of B; 15−25 min, 50−100% volume percentage of B; 25−30 min, 100% volume percentage of B; 30−32 min, 100−20% volume percentage of B; and 32−35 min, 20% volume percentage of B. The flow rate was set at 1 mL min^{-1}, and the column temperature was set at 25 °C using an Agilent G1316A thermostatted column compartment. The ELSD response [(peak area) = a(concentration)^b, with b set at 1.5] was calibrated for D-glucose, D-fructose, and sucrose with five solutions of the authentic substances, covering the range of 0.6−3.0 g L^{-1}.

2.3. Biofuel Potentials. *2.3.1. Enzymatically DOM.* The enzymatically DOM of the biomass, as determined by the De Boever method,[12] was used to compare the suitability of the different biomasses to be converted by anaerobic digestion (biomethanation) without any pretreatment. For the purpose of our study, this method was considered much faster than determining the real biomethane potential, while the results can be correlated with anaerobic digestibility without any pretreatment of the biomass.[12,19] We considered that the enzymatically DOM corresponds to the minimum level of anaerobic digestibility of the biomass without any pretreatment. Indeed, the microbial digestion is expected to produce more enzymes *in situ*, with a broader substrate spectrum than the enzyme cocktail used in the assay. Microbial digestion can also progress for longer periods of time. Briefly, biomass samples were incubated, in chronologic order, with pepsin in 0.1 mol L^{-1} HCl for 24 h at 40 °C,

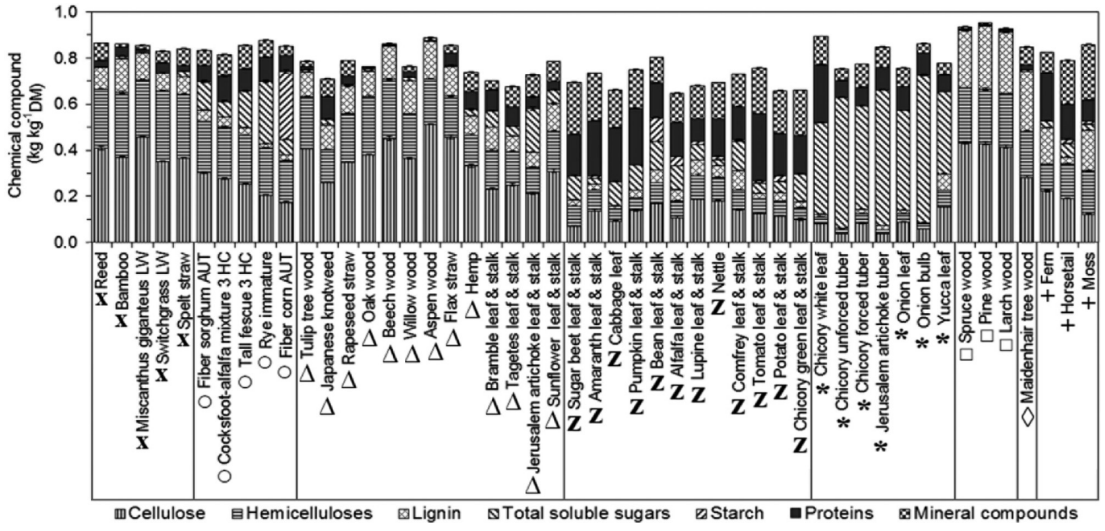

Figure 2. Chemical composition of the analyzed biomasses. Error bars correspond to the standard deviation of the mean. 3HC, 3 harvest cycles; AUT, early autumn; LW, late winter; X, commelinid fibrous biomass; ○, commelinid moderately fibrous biomass; △, non-commelinid fibrous magnoliophyta biomass; Z, non-commelinid moderately fibrous magnoliophyta biomass; *, non-commelinid high total soluble sugar magnoliophyta biomass; □, pinophyta biomass; ◇, ginkgophyta biomass; and +, non-spermatophyta biomass.

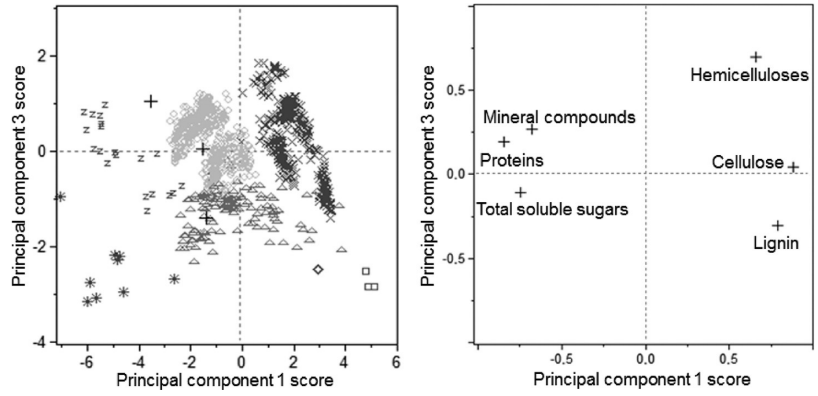

Figure 3. PCA of the chemical composition of the analyzed biomasses. (Left) Scatter plot along the first and third principal components. ×, commelinid fibrous biomass; ○, commelinid moderately fibrous biomass; △, non-commelinid fibrous magnoliophyta biomass; z, non-commelinid moderately fibrous magnoliophyta biomass; *, non-commelinid high total soluble sugar magnoliophyta biomass; □, pinophyta biomass; ◇, ginkgophyta biomass; and +, non-spermatophyta biomass. (Right) Correlation plot along the first and third principal components.

with 0.1 mol L^{-1} HCl for 45 min at 80 °C, and with cellulase in an acetate buffer at pH 4.8 for 24 h at 40 °C.

2.3.2. Bioethanol. The bioethanol potential was calculated as the ethanol that can be expected from fermentation of the directly available soluble sugars and starch and also from cellulose and hemicelluloses after biomass hydrolysis. The bioethanol potential of carbohydrates was assessed by following the methodology by Spatari et al.,[11] on the basis of (1) the monomers expected from the hydrolysis yields of cellulose, hemicelluloses (hydrolysis yields of 91 and 81%, respectively, with a liquid hot water pretreatment[20]), and starch (hydrolysis yield of 96%[21]); (2) the stoichiometric ethanol fermentation yields of monosaccharides (92.5% for glucose and fructose and 86% for xylose, arabinose, galactose, and mannose[22]), and (3) the ethanol recovery yield (99.5%[11]).

2.3.3. Thermal Energy. The thermal energy was assessed on the basis of the HHV. The HHV was determined by the method using a Parr-controlled oxygen bomb calorimeter.[23] The sample was ground, pelletized, and dried for one night at 103 °C. The higher calorific value was then measured using a Parr 6200 calorimeter.

2.4. Statistical Analysis. The principal component analysis (PCA) and the correlation analysis were performed using JMP 7.0.1 (SAS Institute, Cary, NC). The starch content was not included in the PCA because starch was present in only a few biomasses (Figure 1 and Table A1 of the Supporting Information). Therefore, including starch content in the PCA would have biased the results.

Variability of the results was expressed as the standard error of the mean, i.e., the standard deviation divided by the square root of the number of samples, to compare results obtained from different numbers of samples.

3. RESULTS AND DISCUSSION

3.1. Biomass Chemical Composition. The chemical composition of the analyzed biomasses is shown in Figure 2. Details can be found in Table A1 of the Supporting Information. A wide range of values is observed for each main chemical component (Figure 2). Late winter miscanthus, beech wood, and aspen wood are the biomasses with the highest content of cellulose + hemicelluloses. Pinophyta biomasses have the highest content of lignin. The highest contents of soluble sugars (soluble monosaccharides, sucrose, and fructans), proteins, and mineral compounds are observed in onion bulb, tomato leaf and stalk, and moss, respectively.

A PCA was performed on the chemical composition (except starch). Figure 3 plots the results with respect to the first and

dx.doi.org/10.1021/ef3019244 | Energy Fuels 2013, 27, 2588−2598

third principal components. On the basis of the chemical composition (Figure 2) and the PCA (Figure 3), 6 types of biomass profiles are observed (scatter plot of Figure 3): (1) upper right side, commelinid fibrous biomasses (reed, bamboo, miscanthus, switchgrass, and spelt straw) that have high contents of cellulose and hemicelluloses, an intermediate content of lignin, and low contents of non-structural carbohydrates, proteins, and mineral compounds; (2) center and upper left side, commelinid moderately fibrous biomasses [fiber sorghum, "cocksfoot−alfalfa" mixture (mean of 3 harvest cycles), tall fescue (mean of 3 harvest cycles), immature rye, and fiber corn] that have intermediate contents of cellulose, hemicelluloses, lignin, total soluble sugars, proteins, and mineral compounds; (3) lower center side, non-commelinid fibrous magnoliophyta biomasses (tulip tree wood, Japanese knotweed, rapeseed straw, oak wood, beech wood, willow wood, aspen wood, flax straw, hemp, bramble leaf and stalk, tagetes, Jerusalem artichoke leaf and stalk, and sunflower leaf and stalk) that have a high content of lignin and intermediate contents of cellulose, hemicelluloses, total soluble sugars, proteins, and mineral compounds (the woody non-commelinid fibrous magnoliophyta biomasses are the species that are situated on the scatter plot near miscanthus, a commelinid fibrous biomass); (4) left side, non-commelinid moderately fibrous magnoliophyta biomasses (sugar beet leaf and stalk, amaranth, cabbage leaf, pumpkin leaf and stalk, bean leaf and stalk, alfalfa leaf and stalk, lupine leaf and stalk, nettle, comfrey leaf and stalk, tomato leaf and stalk, potato leaf and stalk, and chicory green leaf) that have high contents of proteins and mineral compounds, an intermediate content of total soluble sugars, and low contents of cellulose, hemicelluloses, and lignin; (5) bottom left side, non-commelinid high total soluble sugar magnoliophyta biomasses (chicory white leaf, unforced and forced tuber of chicory, Jerusalem artichoke tuber, leaf and bulb of onion leaf, and yucca leaf) that have a high content of total soluble sugars, intermediate contents of proteins and mineral compounds, and low contents of cellulose, hemicelluloses, and lignin; and (6) bottom right side, pinophyta biomasses (spruce wood, pine wood, and larch wood) that have high contents of cellulose, hemicelluloses, and lignin and low contents of non-structural carbohydrates, proteins, and mineral compounds.

The chemical composition profile of maidenhair tree wood, fern, horsetail, and moss is near those of pinophyta, non-commelinid fibrous magnoliophyta, non-commelinid moderately fibrous magnoliophyta, and commelinid moderately fibrous biomasses, respectively. The three non-spermatophyta biomasses seem to have their own chemical composition profile. This can be explained by the fact that these plants are not magnoliophyta biomasses.

The first and third principal components represent 59.5 and 11.8% of the total variability, respectively (see Table A2 of the Supporting Information). Thus, these two components explain 71.3% of the total variability of the sample composition. The cleavage is mainly explained by the eigenvector of the first principal component (Figure 3 and Table A2 of the Supporting Information) which shows (1) high positive correlations among the contents of structural components (cellulose, hemicelluloses, and lignin) on the one hand and among the contents of non-structural components (total soluble sugars, proteins, and mineral compounds) on the other hand and (2) high negative correlations among the contents of structural components and non-structural components. These correlations can be explained by the fact that biomasses with high contents of structural components are mainly made of stems (rich in secondary cell walls) with more lignified cell walls, whereas biomasses with high contents of non-structural components are also made of an important part of leaves with less lignified cell walls and cytoplasm-rich metabolically active cells.

The cleavage between the defined groups is also explained by the eigenvector of the third principal component (Figure 3 and Table A2 of the Supporting Information), which has a very high positive correlation with the total content of hemicelluloses. This can be explained by the botanical difference in terms of the cell wall components of commelinid and non-commelinid magnoliophyta biomasses. Commelinid biomasses are known to have a higher content of hemicelluloses and a lower content of pectins, as compared to non-commelinid magnoliophyta biomasses.[4,15] Pectins were not analyzed in our study because they are considered as a negligible component of this type of biomass. Fairbrothber et al.[24] and Adam et al.[25] showed that the pectin content of similar biomasses does not exceed 0.06 kg kg^{-1}_{DM}.

The second and fourth principal components are also important components because of their relative eigenvalue percentage (see Table A2 of the Supporting Information). Their eigenvectors correlate mostly with mineral compounds and total soluble sugars, respectively. This means that these two chemical components are also important discrimination parameters for the investigated biomasses.

The significant negative or positive correlations between the contents of chemical components shown by the eigenvector of the first principal component (Figure 3 and Table A2 of the Supporting Information) are confirmed by the results of the correlation analysis of commelinid biomasses and non-commelinid magnoliophyta biomasses (Table A3 of the Supporting Information).

Figure 2 shows a total of 0.10−0.30 kg kg^{-1}_{DM} non-identified components in all biomasses. Two types of non-identified components can be expected:[26] (1) the non-identified structural fraction most likely composed of acid-soluble lignin, soluble structural polysaccharides (such as pectins), and the acetyl groups of hemicelluloses and pectins and (2) the non-identified non-structural fraction most likely composed of organic acids, alcohols, pigments, and lipids.

Moderately fibrous biomasses have a higher non-identified fraction compared to the other biomasses. This can be explained by the higher pectin content and the lower hemicelluloses content in moderately fibrous biomasses, as compared to fibrous biomasses. The latter are indeed mainly made of stems rich in secondary cell walls, whereas moderately fibrous biomasses also have an important part of leaves.[4]

Lipids are not expected to contribute significantly to the non-identified fraction of the biomasses (see section 3.4.3).

Note that the chemical composition of biomasses depends upon the plant development at the harvest time, which is linked to the geographical location (northern hemisphere in our study). Late winter harvested biomasses have higher contents of structural components and lower contents of non-structural components, as compared to the corresponding biomasses harvested during autumn (Figure 2). This can be explained by the nutrient translocation to the rhizomes, the solubilization, and the leaching of the non-structural components during the winter.[27]

3.2. Monosaccharidic Composition of Hemicelluloses.

Figure 4 presents the composition of the hemicelluloses (details

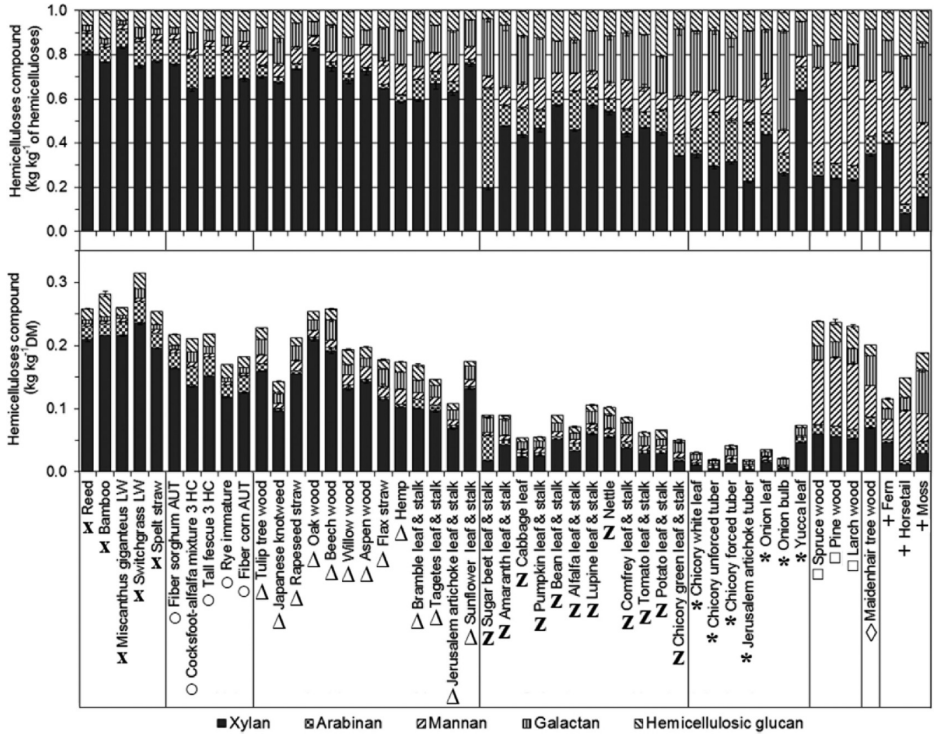

Figure 4. Relative (top) and absolute (bottom) monosaccharidic composition of hemicelluloses of the analyzed biomasses. 3HC, 3 harvest cycles; AUT, early autumn; LW, late winter; X, commelinid fibrous biomass; ○, commelinid moderately fibrous biomass; △, non-commelinid fibrous magnoliophyta biomass; Z, non-commelinid moderately fibrous magnoliophyta biomass; ∗, non-commelinid high total soluble sugar magnoliophyta biomass; □, pinophyta biomass; ◊, ginkgophyta biomass; and +, non-spermatophyta biomass.

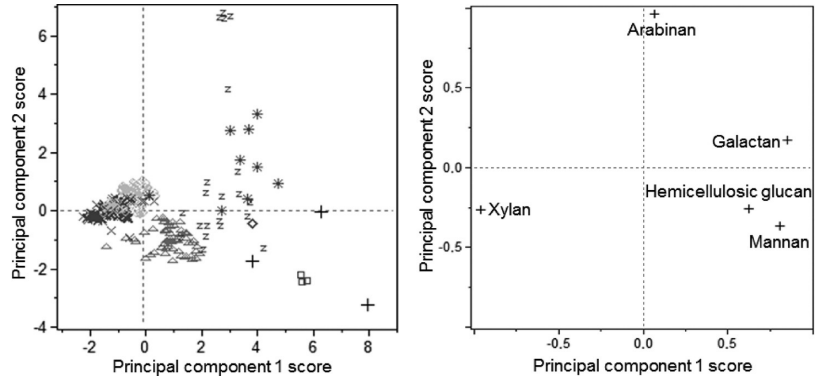

Figure 5. PCA of the relative monosaccharidic composition of hemicelluloses of the analyzed biomasses. (Left) Scatter plot along the first and second principal components. ×, commelinid fibrous biomass; ○, commelinid moderately fibrous biomass; △, non-commelinid fibrous magnoliophyta biomass; z, non-commelinid moderately fibrous magnoliophyta biomass; ∗, non-commelinid high total soluble sugar magnoliophyta biomass; □, pinophyta biomass; ◇, ginkgophyta biomass; and +, non-spermatophyta biomass. (Right) Correlation plot along the first and second principal components.

in Table A4 of the Supporting Information). A wide range of values is observed for the absolute and relative monosaccharidic composition of hemicelluloses (top and bottom of Figure 4, respectively). Commelinoid and non-commelinid fibrous magnoliophyta biomasses have the highest absolute content of hemicelluloses. Xylan is generally the major absolute and relative monosaccharide of hemicelluloses, except in the following biomasses: (1) sugar beet leaf and stalk, where arabinan is the highest absolute and relative hemicellulosic component; (2) high total soluble sugar biomasses (leaf and bulb of onion, yucca leaf, Jerusalem artichoke tuber, chicory white leaf, and unforced and forced tuber of chicory), where galactan and arabinan are also high relative hemicellulosic components; and (3) less evolved species, pinophyta (spruce wood, pine wood, and larch wood) and non-spermatophyta (maidenhair tree wood, fern horsetail, and moss) biomasses, where mannan is also a high absolute and relative hemicellulosic component.

A PCA was performed on the relative monosaccharidic composition of hemicelluloses. Figure 5 plots the results with respect to the first and second principal components, which help to distinguish 3 types of biomass profiles (scatter plot of Figure 5): (1) upper left center side, commelinid biomasses (reed, bamboo, miscanthus, switchgrass, fiber sorghum, fiber corn, spelt straw, tall fescue, "cocksfoot−alfalfa" mixture, and immature rye), where the major relative hemicellulosic

dx.doi.org/10.1021/ef3019244 | Energy Fuels 2013, 27, 2588−2598

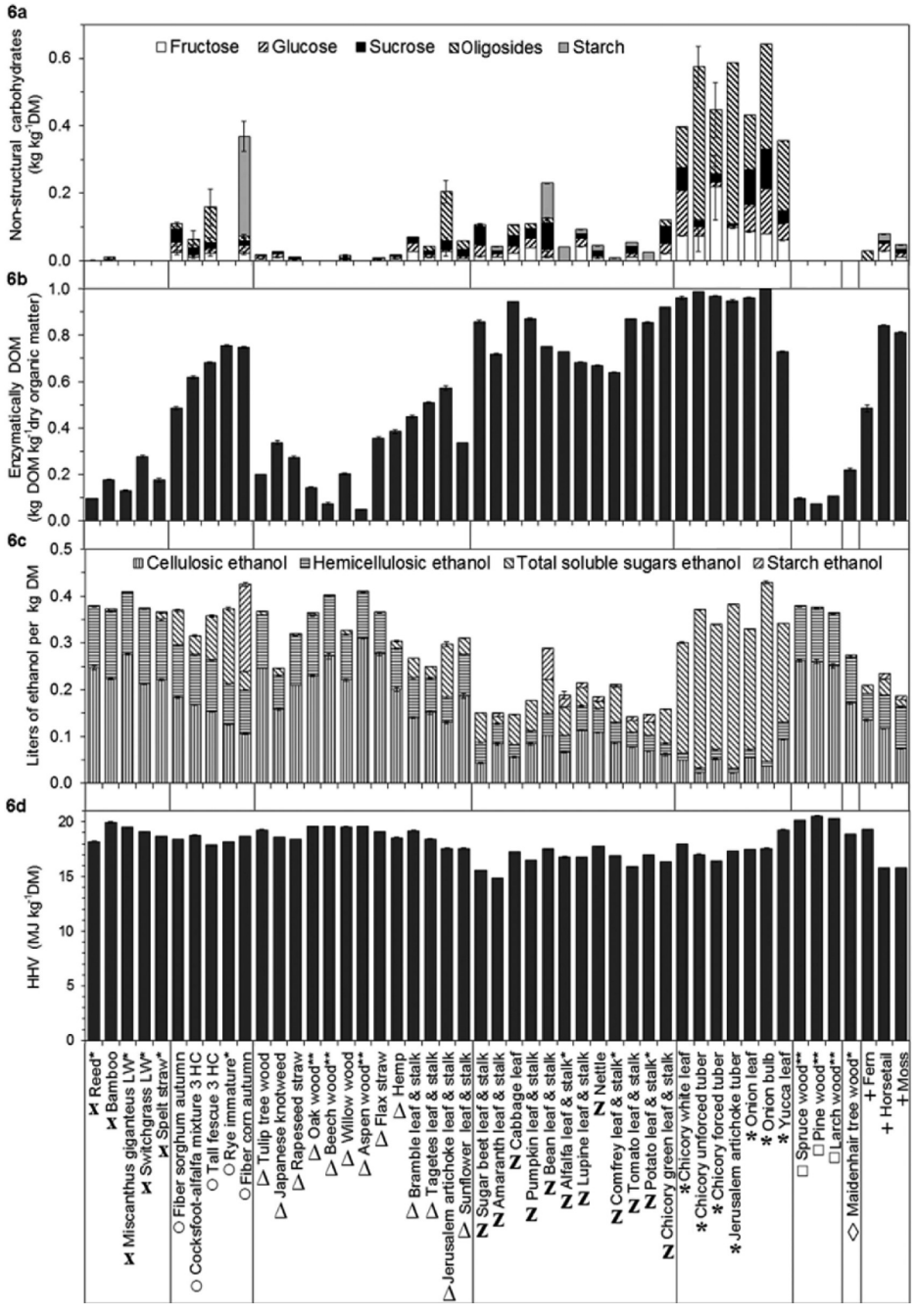

Figure 6. (a) Identified saccharides that contribute to the total soluble sugars, (b) enzymatically DOM of the analyzed biomasses, (c) potential bioethanol of the analyzed biomasses, and (d) HHV of the analyzed biomasses in the dry state. Error bars correspond to the standard deviation of the mean: (∗) fructose, glucose, sucrose, and oligosides not determined and (∗∗) fructose, glucose, sucrose, and oligosides not detected. 3HC, 3 harvest cycles; AUT, early autumn; LW, late winter; X, commelinid fibrous biomass; ○, commelinid moderately fibrous biomass; △, non-commelinid fibrous magnoliophyta biomass; Z, non-commelinid moderately fibrous magnoliophyta biomass; ∗, non-commelinid high total soluble sugar magnoliophyta biomass; □, pinophyta biomass; ◊, ginkgophyta biomass; and +, non-spermatophyta biomass.

components are generally, by order of decreasing importance, xylan, arabinan, hemicellulosic glucan, galactan, and mannan (commelinid monocotyledons are known to have higher contents of arabinoxylan and β-glucan, as compared to non-commelinid magnoliophyta biomasses);[4] (2) lower right center and right side gathers non-commelinid magnoliophyta biomasses, either fibrous (tulip tree wood, Japanese knotweed, rapeseed straw, oak wood, beech wood, willow wood, aspen wood, flax straw, hemp, bramble leaf and stalk, tagetes, Jerusalem artichoke leaf and stalk, and sunflower leaf and stalk), moderately fibrous (sugar beet leaf and stalk, amaranth, cabbage leaf, pumpkin leaf and stalk, bean leaf and stalk, alfalfa leaf and stalk, lupine leaf and stalk, nettle, comfrey leaf and stalk, tomato leaf and stalk, potato leaf and stalk, and chicory green leaf), or with high total soluble sugars (chicory white leaf, unforced and forced tuber of chicory, Jerusalem artichoke tuber, leaf and bulb of onion leaf, and yucca leaf) (In these biomasses, the relative xylan content of hemicelluloses is generally lower and the relative contents of hemicellulosic glucan, galactan, and mannan are generally higher, as compared

dx.doi.org/10.1021/ef3019244 | Energy Fuels 2013, 27, 2588−2598

Table 1. Cross-correlations between the Enzymatically DOM, Bioethanol Potential from Structural Carbohydrates, Bioethanol Potential from Non-structural Carbohydrates, HHV, and Chemical Composition of Commelinid (n = 873) and Non-commelinid (n = 179) Magnoliophyta Biomasses

	cellulose	hemicelluloses	lignin	total soluble sugars	proteins	mineral compounds
Commelinid Magnoliophyta						
enzymatically DOM	−0.94[a]	−0.76[a]	−0.94[a]	0.69[a]	0.80[a]	0.38[a]
bioethanol from structural carbohydrates	0.97[a]	0.82[a]	0.92[a]	−0.60[a]	−0.69[a]	−0.27[a]
bioethanol from non-structural carbohydrates	−0.89[a]	−0.80[a]	−0.80[a]	0.48[a]	0.43[a]	−0.04[b]
HHV	0.59[a]	0.48[a]	0.73[a]	−0.73[a]	−0.71[a]	−0.80[a]
Non-commelinid Magnoliophyta						
enzymatically DOM	−0.89[a]	−0.75[a]	−0.87[a]	0.63[a]	0.60[a]	0.74[a]
bioethanol from structural carbohydrates	0.98[a]	0.89[a]	0.86[a]	−0.69[a]	−0.57[a]	−0.64[a]
bioethanol from non-structural carbohydrates	−0.69[a]	−0.65[a]	−0.66[a]	0.99[a]	−0.01[b]	0.06[b]
HHV	0.65[a]	0.51[a]	0.70[a]	−0.48[a]	−0.30[a]	−0.72[a]

[a] $p < 0.001$. [b] No significant p value.

to commelinid biomasses. Non-commelinid magnoliophyta are known to have hemicelluloses with higher contents of xyloglucan and mannan compared to commelinid biomasses.[4] In Figure 5, the non-commelinid magnoliophyta group tends to be subdivided according to the chemical composition in the 3 following subgroups: non-commelinid fibrous magnoliophyta, non-commelinid moderately fibrous magnoliophyta, and non-commelinid high total soluble sugar magnoliophyta. This subdivision corresponds to the increasing relative contents of arabinan and galactan of hemicelluloses. Sugar beets leaf and stalk are the biomasses that are at the right top part of the scatter plot because of their very high relative content of arabinan in hemicelluloses); and (3) bottom right side, pinophyta (spruce wood, pine wood, and larch wood), ginkgophyta (maidenhair tree wood), and non-spermatophyta biomasses (fern, horsetail, and moss), where the relative contents of xylan and mannan in hemicelluloses are low and high, respectively, as compared to the magnoliophyta biomasses (Pinophyta biomasses are known to have hemicelluloses with a higher content of mannan, as compared to magnoliophyta biomasses.[4] Fern is the biomass for which this is the least pronounced).

The first and second principal components represent 54.5 and 24.6% of the total variability, respectively (see Table A5 of the Supporting Information). Thus, these two components explain 79.1% of the total variability of the sample composition. The cleavage is mainly explained by the eigenvector of the first principal component (Figure 5 and Table A5 of the Supporting Information), which shows (1) high positive correlations among the relative contents of mannan, galactan, and hemicellulosic glucan in hemicelluloses and (2) high negative correlation among the relative content of xylan in hemicelluloses. These correlations can be explained by the fact that the contents of xyloglucan (which also contains galactan and hemicellulosic glucan), mannan (which also contains galactan and hemicellulosic glucan), and β-glucan and the content of arabinoxylan are high and low, respectively, in less lignified cell walls (poor in secondary cell walls), as compared to more lignified cell walls.[9,10] The cleavage between these groups is also explained by the eigenvector of the second principal component (Figure 5 and Table A5 of the Supporting Information), which has a very high positive correlation with the relative content of arabinan in hemicelluloses. This can be explained by the botanical difference in terms of the cell wall hemicellulosic components of commelinid and non-commelinid magnoliophyta biomasses. Commelinid biomasses are known to have a higher content of arabinoxylan, as compared to non-commelinid magnoliophyta biomasses. The latter have a higher content of xyloglucan and mannan.[9,10] The third principal component of the PCA is also important because of its relative eigenvalue percentage (Figure 5 and Table A5 of the Supporting Information) and its high positive correlation with the relative content of hemicellulosic glucan. This means that this hemicellulosic component is also an important discrimination parameter for the investigated biomasses.

The significant negative or positive correlations between the relative contents of hemicellulosic xylan, mannan, galactan, and glucan shown by the eigenvector of the first principal component (Figure 5 and Table A5 of the Supporting Information) are confirmed by the results of the correlation analysis of commelinid biomasses and non-commelinid magnoliophyta biomasses (see Table A6 of the Supporting Information). The high correlation between the relative content of hemicellulosic xylan and arabinan (see Table A6 of the Supporting Information) can be explained by the fact that less lignified cell walls (with lower contents of structural components, poor in secondary cell walls) are known to have arabinoxylan with a higher degree of substitution by arabinan and higher contents of xyloglucan, β-glucan, and mannan, as compared to more lignified cell walls, which have a higher content of arabinoxylan with a lower degree of substitution by arabinan.[4,9,10] This can also explain the high positive correlation between the relative content of hemicellulosic arabinan and galactan and the high positive correlation between hemicellulosic xylan and glucan in commelinid biomasses (see Table A6 of the Supporting Information).

3.3. Soluble and Reserve Carbohydrates. The mono-, di-, and oligosaccharides that contribute to the total soluble carbohydrates were further characterized for the various biomasses. Figure 6a presents the total concentration of easily fermentable carbohydrates that can be collected when harvesting the different biomasses under the specified conditions. In late winter, no soluble carbohydrates were detected. In Jerusalem artichoke and chicory, oligosaccharides up to a degree of polymerization of 25−30 were detected (data not shown). They were most likely fructooligosides.[28] These oligosaccharides peaks were also detected in the LC chromatograms of spelt, fiber sorghum, cocksfoot−alfalfa, tall fescue, rapeseed, bramble, amaranth, cabbage, pumpkin, bean, lupine, nettle, tomato, chicory, onion, yucca, and horsetail.

3.4. Biomass Characteristics as a Guide in the Selection of Transformation Technology. *3.4.1. Enzymati-*

dx.doi.org/10.1021/ef3019244 | Energy Fuels 2013, 27, 2588−2598

Table 2. Cross-correlations between the Enzymatically DOM, Bioethanol Potential from Structural Carbohydrates, Bioethanol from Non-structural Carbohydrates, and HHV of Commelinid (n = 873) and Non-commelinid (n = 179) Magnoliophyta Biomasses

	enzymatically DOM	bioethanol potential from structural carbohydrates	bioethanol potential from non-structural carbohydrates	HHV
		Commelinid Magnoliophyta		
enzymatically DOM				
bioethanol potential from structural carbohydrates	−0.96[a]			
bioethanol potential from non-structural carbohydrates	0.85[a]	−0.93[a]		
HHV	−0.67[a]	0.62[a]	−0.41[a]	
		Non-commelinid Magnoliophyta		
enzymatically DOM				
bioethanol potential from structural carbohydrates	−0.97[a]			
bioethanol potential from non-structural carbohydrates	0.72[a]	−0.71[a]		
HHV	−0.70[a]	0.68[a]	−0.47[a]	

[a] $p < 0.001$.

cally DOM. The enzymatically DOM was used to assess the suitability of the analyzed biomasses for anaerobic digestion (biomethanation) without any pretreatment. Figure 6b (details in Table A7 of the Supporting Information) shows that the investigated biomasses offer a wide range of enzymatically DOM per kilogram of dry organic matter. The biomasses with the highest enzymatically DOM are those that are moderately fibrous and/or that have a high content of total soluble sugars. This can be explained by their high total soluble sugar, starch, and/or protein contents, which are a part of the enzymatically DOM.[12] These biomasses are made of an important part of cells with high contents of non-structural components and less lignified cell walls (Figure 2). Biomasses with high enzymatically DOM have generally a high content of mineral compounds (Figures 2 and 6b). Indeed, they are made of an important part of leaves that have much less lignified cell walls and their cells are rich in cytoplasm that contains the mineral salts.

The correlations between the enzymatic digestibility and the chemical composition show that the enzymatically DOM has high significant positive and negative correlations with non-structural and structural components, respectively (Table 1). Non-structural components are clearly more digestible than structural components.

3.4.2. Bioethanol. Figure 6c (details in Table A7 of the Supporting Information) shows the calculated bioethanol production that can be expected from the analyzed biomasses. Bioethanol production from soluble carbohydrates and starch/fructanes can be readily fermented with current technologies, whereas bioethanol production from cellulose and hemicelluloses needs a biomass pretreatment to be fermented. A wide range of total bioethanol potential is observed in Figure 6c. The biomasses with the highest total bioethanol potential are commelinid, non-commelinid fibrous magnoliophyta, non-commelinid high total soluble sugar magnoliophyta, and pinophyta biomasses because of their high contents of structural and non-structural carbohydrates (Figure 2). Commelinid fibrous, non-commelinid fibrous magnoliophyta, ginkgophyta, and pinophyta biomasses (Figure 6c) offer the structural carbohydrate bioethanol potential, owing to their high contents of cellulose and hemicelluloses (Figure 2). Non-commelinid high total soluble sugar magnoliophyta biomasses offer the highest non-structural carbohydrate bioethanol potential (Figure 2). The bioethanol potential results mainly from the conversion of structural carbohydrates to ethanol, except for (Figure 6c): (1) non-commelinid high total soluble sugar magnoliophyta biomasses (they offer the highest non-structural carbohydrate bioethanol potential; the conversion of non-structural carbohydrates to bioethanol constitutes a huge part of the total bioethanol potential) and (2) some commelinid moderately fibrous biomasses (immature rye and fiber corn), where the conversion of non-structural carbohydrates to bioethanol also constitutes an important part of the total bioethanol potential. On the basis of data by Patzek et al.,[29] the bioethanol potential of sugar cane (*Saccharum officinarum* L.) stems would be part of this group of biomasses. It has a bioethanol potential resulting from structural carbohydrates and non-structural carbohydrates of 231 and 293 L of ethanol/kg of DM, respectively.

There are highly significant positive and negative correlations between the structural components and the bioethanol coming from structural carbohydrates and non-structural carbohydrates, respectively (Table 1). This is a direct consequence of the correlations discussed in Table A3 of the Supporting Information.

3.4.3. Thermal Energy. The HHV was used to assess the suitability of the biomasses for conversion to thermal energy by combustion, independent of their humidity (that can be adjusted by drying, if required). Figure 6d (details in Table A7 of the Supporting Information) shows that the HHV of all analyzed biomasses falls in a narrow range. HHV depends mainly upon the total organic matter, which is the complement to mineral compounds (on the basis of the correlation analysis of Table 1) for which a narrow range is also observed (Figure 2). Fibrous biomasses offer the highest HHV.

The highest significant correlation between the HHV and the chemical composition is the negative correlation with the mineral compounds (Table 1). The relatively low content of lignin (HHV of 25.1 MJ kg^{-1} dry lignin[30]) and proteins (HHV of 24.0 MJ kg^{-1} dry protein[30]) of the organic matter (complement of the mineral compounds) and the relatively low differences of HHV between the other individual organic compounds (monosaccharides of 15.6 MJ kg^{-1} dry monosaccharide and polysaccharides of 17.5 MJ kg^{-1} dry

dx.doi.org/10.1021/ef3019244 | *Energy Fuels* 2013, 27, 2588−2598

polysaccharide[30]) can explain this correlation. Biomasses with a high HHV are mainly made of stems that have high organic matter (and low mineral compounds) contents and more lignified cell walls. Biomasses with a low HHV are made of an important part of leaves that have cytoplasm-rich, less lignified cells.

Biomass with a significant content of lipids would have a much higher HHV because lipids have a high specific HHV (lipids of 39.8 MJ kg^{-1} dry lipids[30]). This is not observed among the analyzed biomasses. This confirms that lipids are a negligible component of these biomasses (Figure 6d and Table A7 of the Supporting Information).

There is also a high significant negative correlation between the HHV and the enzymatically DOM (Table 2). This is consistent with the negative influence of lignified structural components on DOM (Table 1).

3.4.4. Biomass Clusters for the Biofuel Potentials. Table 1 show that the analyzed biofuel potentials generally have a high significant correlation with the biomass chemical composition. Therefore, we extrapolated the 6 clusters of the biomass chemical compositions (section 3.1) to the biofuel potentials. As shown in Figure 2 and panels b−d of Figure 6 (details in Table A7 of the Supporting Information), the biofuel potentials can be divided into fibrous and moderately fibrous biomasses. These groups tend to be subdivided according to the phylogenetic origin of the biomasses (commelinid monocots, non-commelinid magnoliophyta, and pinophyta biomasses). These clusters can be used to classify vegetal biomasses into categories corresponding to the biofuel conversion pathways that suit them the most. Fibrous biomasses have high suitabilities to be used as solid biofuel for combustion or to be converted into bioethanol coming from cellulose and hemicelluloses (Figure 2 and panels c and d of Figure 6 and Tables A1 and A5 of the Supporting Information). Moderately fibrous biomasses have high suitabilities to be converted by anaerobic digestion or to be converted into bioethanol, except for the non-commelinid moderately fibrous group, which has a low suitability for this conversion (Figure 2 and panels b and c of Figure 6 and Tables A1 and A5 of the Supporting Information).

4. CONCLUSION

The investigation of a wide diversity of plant types revealed a wide diversity of compositions, at the level of both the chemical composition and the monosaccharidic composition of hemicelluloses. Despite this diversity, the dry state HHV of these biomasses remained in a narrow range (16−20 MJ kg^{-1}_{DM}), mostly affected by the biomass content in organic matter (complement of the mineral compounds). The biomass enzymatic digestibility, used to predict the anaerobic digestibility, ranges from 5 to 100% of the organic matter. Biomasses with lower structural carbohydrates, which correlate with lower lignification, appear better suited to digestion than fibrous biomasses. The biomasses with a high content of non-structural carbohydrates offer bioethanol potentials in the range of 0.1−0.3 L_{EtOH} kg^{-1}_{DM}. When considering the conversion of structural carbohydrates to ethanol, many biomasses can offer bioethanol potentials in the range of 0.1−0.4 L_{EtOH} kg^{-1}_{DM}. The PCAs revealed that plant biomasses, both at the level of their chemical composition and the monosaccharidic composition of their hemicelluloses, can be clustered into groups that correspond to phylogenetic groups: commelinid monocots, non-commelinid magnoliophyta, and pinophyta biomasses. The clustering also distinguished fibrous and moderately fibrous biomasses. These analyses showed the parameters that discriminate the investigated biomasses: (1) Commelinid biomasses are distinguished from non-commelinid magnoliophyta biomasses by high contents of xylan + arabinan in the hemicelluloses and total hemicelluloses. (2) Pinophyta biomasses are distinguished from more evolved biomasses (magnoliophyta) by very high contents of hemicellulosic mannan and lignin. (3) The content of mineral compounds contributes significantly to the cleavage between fibrous and moderately fibrous biomasses, probably in connection with the presence of cells rich in cytoplasm (containing the mineral salts) in the moderately fibrous biomasses.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Chemical composition (mean and standard deviation of the mean) of the analyzed biomasses (Table A1), eigenvalue relative percentage and eigenvector of the PCA of the chemical composition of the analyzed biomasses (Table A2), cross-correlations between the contents of the main chemical components of the commelinid (n = 873) and non-commelinid (n = 179) magnoliophyta biomasses (Table A3), absolute monosaccharidic composition of hemicelluloses (mean and standard deviation of the mean) of the analyzed biomasses (Table A4), eigenvalue relative percentage and eigenvector of the PCA of the relative monosaccharidic composition of hemicelluloses of the analyzed biomasses (Table A5), cross-correlations between the relative monosaccharidic composition of hemicelluloses of the commelinid (n = 211) and non-commelinid (n = 99) magnoliophyta biomasses (Table A6), and enzymatically DOM, bioethanol potential, and HHV (mean and standard deviation of the mean) of the analyzed biomasses (Table A7). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: 00-32-81-61-58-47. E-mail: b.godin@cra.wallonie.be.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was funded by the Walloon Agricultural Research Center (CRA-W) with the support of the Belgian Science Policy and by the ENERBIOM project (ENERBIOM project 14GR23024 of the European territorial co-operation program in the context of INTERREG IV A "Grande Région" 2007−2013, CCI2007CB163PO064, co-financed by the FEDER-EU funds). The authors are grateful to the technicians of the BIOETHA2 and the ENERBIOM projects for their technical support.

■ NOMENCLATURE

ADL = acid detergent lignin
asl = above sea level
AUT = autumn
DM = dry matter
DOM = digestible organic matter
ELSD = evaporative light scattering detector
HC = harvest cycle
HHV = higher heating value

LC = liquid chromatography
LW = late winter
PCA = principal component analysis
SAH = sulfuric acid hydrolysis
VS = Van Soest

REFERENCES

(1) European Union.. *Off. J. Eur. Union* **2003**, *L123*, 42−46.
(2) McKendry, P. *Bioresour. Technol.* **2002**, *83*, 37−46.
(3) Ghysel, F.; Godin, B.; Flamin, C.; Delfosse, P.; Delcarte, J.; Stilmant, D. *Fourrages* **2010**, *203*, 163−173.
(4) Carpita, N.; McCann, M. *Biochemistry and Molecular Biology of Plants*; American Society of Plant Physiologists: Rockville, MD, 2000; pp 52−108.
(5) Pauly, M.; Keegstra, K. *Plant J.* **2008**, *54*, 559−568.
(6) Chandel, A.; Singh, O.; Rao, L. *Sustainable Biotechnology: Sources of Renewable Energy*; Springer: New York, 2010; pp 63−81.
(7) Kamm, B.; Kamm, M. *Appl. Microbiol. Biotechnol.* **2004**, *64*, 137−145.
(8) Saidur, R.; Abdelaziz, E.; Demirbas, A.; Hossain, M.; Mekhilef, S. *Renewable Sustainable Energy Rev.* **2011**, *15*, 2262−2289.
(9) Ishii, T. *Plant Sci.* **1997**, *127*, 111−127.
(10) Vogel, J. *Curr. Opin. Plant Biol.* **2008**, *11*, 301−307.
(11) Spatari, S.; Bagley, D.; MacLean, H. *Bioresour. Technol.* **2010**, *101*, 654−667.
(12) De Boever, J.; Cottyn, B.; Andries, J.; Buysse, F.; Vanacker, J. *Anim. Feed Sci. Technol.* **1988**, *19*, 247−260.
(13) De Boever, J.; Cottyn, B.; Buysse, F.; Vanacker, J. *Anim. Feed Sci. Technol.* **1986**, *14*, 203−214.
(14) Campbell, N.; Reece, J. *Biologie*, 2nd ed.; De Boeck Université: Brussels, Belgium, 2004; pp 649−668.
(15) Godin, B.; Agneessens, R.; Gerin, P.; Delcarte, J. *Talanta* **2011**, *85*, 2014−2026.
(16) Van Soest, P. J. *J. AOAC Int.* **1973**, *56* (4), 781−784.
(17) European Union.. *Off. J. Eur. Union* **2009**, *L54*, 1−130.
(18) Association of Official Analytical Chemists (AOAC). *Official Methods of Analysis*, 15th ed.; AOAC: Washington, D.C., 1990.
(19) Lesteur, M.; Latrille, E.; Maurel, V.; Roger, J.; Gonzalez, C.; Junqua, G.; Steyer, J. *Bioresour. Technol.* **2011**, *102*, 2280−2288.
(20) da Costa Sousa, L.; Chundawat, S.; Balan, V.; Dale, B. *Curr. Opin. Plant Biol.* **2009**, *20*, 1−9.
(21) Buchholz, K.; Seibel, J. *Carbohydr. Res.* **2008**, *343*, 1966−1979.
(22) Hamelinck, C.; van Hooijdonk, G.; Faaij, A. *Biomass Bioenergy* **2005**, *28*, 384−410.
(23) European Committee for Standardization (CEN). *CEN/TS 14918: Solid Biofuels—method for the Determination of Calorific Value*; CEN: Brussels, Belgium, 2005.
(24) Fairbrothber, T.; Brink, G. 1990. *Anim. Feed Sci. Technol.* **1990**, *28*, 293−302.
(25) Adam, P.; Ashley, P.; Chum, H.; Deutch, S.; Fennell, J.; Johnson, D. K.; Wiselogel, A. *Study of Compositional Changes in Biomass Feedstocks upon Storage*; Swedish University of Agricultural Sciences: Uppsala, Sweden, 1994; pp 28−52.
(26) Hames, B. *Methods in Molecular Biology*; Humana Press: New York, 2009; Vol. *581*, pp 145−183.
(27) Cadoux, S.; Preudhomme, M.; Machet, J.; Mary, B.; Fourdinier, E.; Ferchaud, F.; Boizard, H.; Gosse, G. *17th European Biomass Conference and Exhibition*; ETA Florence: Florence, Italy, 2019.
(28) Downes, K.; Terry, L. *Talanta* **2010**, *82*, 118−124.
(29) Patzek, T.; Pimentel, D. *Crit. Rev. Plant Sci.* **2005**, *24*, 327−3640.
(30) Klass, D. *Encycl. Energy* **2004**, *1*, 23−212.