Industrial Crops and Products 48 (2013) 1–12

Contents lists available at SciVerse ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Chemical characteristics and biofuel potential of several vegetal biomasses grown under a wide range of environmental conditions

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

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

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

ARTICLE INFO

Article history:
Received 26 November 2012
Received in revised form 25 March 2013
Accepted 8 April 2013

Keywords:
Fibrous biomasses
Carbohydrates
Cellulose
Hemicelluloses
Renewable energy

ABSTRACT

The chemical characteristics of 95 miscanthus giganteus (*Miscanthus* × *giganteus* J.M. Greef & Deuter ex Hodk. & Renvoize), 150 switchgrass (*Panicum virgatum* L.), 79 spelt straw (*Triticum aestivum* L. ssp. *spelta* (L.) Thell.), 145 fiber sorghum (*Sorghum bicolor* (L.) Moench), 27 "cocksfoot–alfalfa" mixture (*Dactylis glomerata* L.–*Medicago sativa* L.), 175 tall fescue (*Festuca arundinacea* Schreb.), 54 immature rye (*Secale cereale* L.), 146 fiber corn (*Zea mays* L.), 80 hemp (*Cannabis sativa* L.) and 46 jerusalem artichoke (*Helianthus tuberosus* L.) independent fibrous biomass samples are summarized in the present paper. Analyzed biomasses show 2 distinctive patterns at the level of both the chemical and hemicellulosic composition. The individual composition for each type of biomass is relatively constant despite the diversity of the crop conditions (year, area, cultivar, nitrogen fertilization level). Fiber corn harvested in autumn offers the highest potential for both digestible organic matter and total bioethanol, owing to its high dry biomass yield, high structural carbohydrates and starch contents and high digestibility. Both fiber corn and miscanthus harvested in autumn offer the highest energy yields per unit area (hm^2) (as higher heating values), owing to their significantly higher dry biomass yield as compared to the other crops. In all cases, autumn harvest offers better yields than late winter harvest, mainly due to a loss of harvestable biomass during winter, and not significantly due to the evolution of their composition.

1. Introduction

The development of the production of vegetal biomasses and of their use as energy source is currently encouraged in the European Union in the context of the European Directive 2003/30/CE (Commission of the European Communities, 2003). The aim of this directive is to produce renewable and sustainable energy allowing the reduction of the greenhouse gas production and the fossil fuel dependence of the European Union. Whole vegetal biomasses are expected to be converted into biofuels (e.g. solid biofuels for combustion, bioethanol or biogas) in the future (Bessou et al., 2011). Sustainability of these biomass-based biofuel productions requires (McKendry, 2002): high dry biomass yield per area unit (hm^2), high biomass availability, low input requirements (fertilizers, pesticides and energy), low environmental impacts on biodiversity, soil and water quality, low greenhouse gas production, low cost.

Two types of crops are investigated within this context: perennial and annual crops. Perennial crops such as miscanthus (*Miscanthus* sp.), switchgrass (*Panicum virgatum* L.), meadows that can be grown on marginal lands (Godin et al., 2010; ENERBIOM, 2012). The growth of meadows harvested several times per year has a higher input requirement than miscanthus and switchgrass. Indeed, miscanthus and switchgrass are harvested at the end of the winter with a high dry matter but low mineral content, as compared to meadows harvested several times per year (Cadoux et al., 2010; ENERBIOM, 2012). Annual crops such as fiber sorghum, fiber corn, cereal straw and hemp. They need higher inputs, better soils and to be reseeded each year, but they do not mobilize a field for more than one cropping year (Cadoux et al., 2010; ENERBIOM, 2012).

Abbreviations: ADF, acid detergent fiber residue; ADL, acid detergent lignin; AUT, autumn; DM, dry matter; DOM, digestible organic matter; ELSD, evaporative light scattering detector; HHV, higher heating value; LC, liquid chromatography; LW, late winter; NDF, neutral detergent fiber residue; RMSE, root mean square error; SAH, sulfuric acid hydrolysis; VS, Van Soest; WM, wet matter.

* Corresponding author at: Walloon Agricultural Research Center – CRA-W, Valorisation of Agricultural Products Department – Biomass, Bioproducts and Energy Unit, Chaussée de Namur, 146, B-5030 Gembloux, Belgium. Tel.: +32 81 62 71 40; fax: +32 81 61 58 47.

E-mail addresses: b.godin@cra.wallonie.be, godin.b@gmail.com (B. Godin).

0926-6690/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.indcrop.2013.04.007

Vegetal biomasses such as forage crops, agricultural residues and wood are mostly made of two types of structural polysaccharides: cellulose and hemicelluloses. Cellulose is a linear polysaccharide homogeneously made of D-glucose units and represents 25–40% of the vegetal biomass dry matter (DM) (Carpita and McCann, 2000). Hemicelluloses are ramified heterogeneous polysaccharides mainly made of linked D-xylose, L-arabinose, D-mannose, D-galactose and D-glucose units and represent 10–30% of the vegetal biomass DM (Carpita and McCann, 2000). The monosaccharidic content of hemicelluloses depends on the plant species (Carpita and McCann, 2000). The hemicelluloses of commelinid monocotyledon biomasses have higher contents of xylan and arabinan, associated as arabinoxylan, and β-glucan (Carpita and McCann, 2000). The hemicelluloses of non-commelinid dicotyledon biomasses have higher contents of hemicellulosic glucan, in the form of xyloglucan, and mannan (Carpita and McCann, 2000). Vegetal biomasses are also made of lignin (phenyl propanoid polymer composed of syringyl, guaiacyl and p-hydroxyphenyl units), pectins (ramified heterogeneous structural polysaccharide mainly composed of D-galacturonic acid units), starch, soluble sugars (D-glucose, D-fructose, sucrose and fructans), proteins and mineral compounds (Carpita and McCann, 2000; Pauly and Keegstra, 2008). All these components (except mineral compounds) represent the largest pool in nature of organic carbon coming from the photosynthetically collected and stored solar energy (Chandel et al., 2010). They represent therefore a huge amount of renewable resource for a sustainable bio-based economy. However, the optimal valorization of biomass to bioproducts and biofuels requires a good knowledge of their molecular composition, in quantity and quality (McKendry, 2002; Kamm and Kamm, 2004).

Vegetal biomasses can be converted to solid (e.g. pellets), liquid (e.g. bioethanol) or gaseous (e.g. biogas) biofuels (Ghysel et al., 2010; Bessou et al., 2011). There are two main conversion routes for the production of these biofuels (Bessou et al., 2011): biochemical conversions (e.g. methanogenic and ethanolic fermentations) and thermochemical conversions (e.g. combustion, gasification and pyrolysis). There are 3 types of energy vectors that can be produced from the ultimate conversion of the biofuels (Bessou et al., 2011): thermal, electricity and mechanical energy. We decided to rapidly compare the energy value of biomasses by comparing (i) their higher heating values (HHV), for combustion (McKendry, 2002), (ii) their bioethanol potentials calculated following the methodology of Spatari et al. (2010), (iii) their enzymatically digestible organic matter (DOM) following the methodology of De Boever et al. (1986), as an assessment of the anaerobic digestibility potential (biomethanation).

The objective of the study reported here is to assess, on large sample sets, the main chemical components of several fibrous biomasses. This composition includes cellulose, hemicelluloses, lignin, total soluble sugars, starch, proteins and mineral compounds, but also the absolute and relative monosaccharidic contents of hemicelluloses (xylan, arabinan, mannan, galactan and hemicellulosic glucan). Variability of the biomass composition was also investigated. The enzymatically DOM, the total bioethanol potential and the HHV of the various biomasses were also determined. The analyzed biomass were miscanthus giganteus, switchgrass, spelt straw, fiber sorghum, "cocksfoot–alfalfa" mixture, tall fescue, immature rye, fiber corn, hemp and jerusalem artichoke crops coming from different trials performed under different conditions (year, area, cultivar, nitrogen fertilization level) and harvest periods (autumn and late winter). The goal of this paper is also to investigate the correlation between biomass chemical composition and the corresponding enzymatically DOM, bioethanol and thermal energy potential.

2. Materials and methods

2.1. Biomass material

Miscanthus giganteus (*Miscanthus* × *giganteus* J.M. Greef & Deuter ex Hodk. & Renvoize), switchgrass (*P. virgatum* L.), fiber sorghum (*Sorghum bicolor* (L.) Moench), spelt straw (*Triticum aestivum* L. ssp. *spelta* (L.) Thell.), "cocksfoot–alfalfa" mixture (*Dactylis glomerata* L.–*Medicago sativa* L.), tall fescue (*Festuca arundinacea* Schreb.), immature rye (*Secale cereale* L.), fiber corn (*Zea mays* L.), hemp (*Cannabis sativa* L.) and jerusalem artichoke (*Helianthus tuberosus* L.; leaf & stalk) came from randomized blocks designed crop trials performed in 2007, 2008, 2009 and/or 2010 at Gembloux (Belgium), Libramont (Belgium), Tinlot (Belgium), Gerbéviller (France) or Mötsch (Germany). Details about the investigated fibrous biomasses and the cropping sites are presented, respectively, in Tables 1 and 2. Depending on the crop, trials were performed with different nitrogen fertilization levels (from 0 to 240 kg of nitrogen per hm^2), different cultivars (details in Table 1) and/or different harvest periods (early autumn or late winter). For each biomass sample, a plot between 9 and 24 m^2 of the whole above ground biomass was harvested and chopped at 10 cm from the ground with a Haldrup M-65 harvester. Nine hundred ninety seven biomass samples were analyzed.

Immediately after the harvest, two representative subsamples of 750 g of the whole of each biomass were 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 were 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 expressed in kg per kg of DM (103 °C dried matter).

The neutral detergent fiber residue (NDF: weight of the neutral detergent fiber residue) was determined by the Van Soest (VS) gravimetric method (Van Soest and Wine, 1967) except that 16.67 $\mu kat\, g^{-1}_{DM\_sample}$ of an analytical thermostable α-amylase (Megazyme, Ireland) was added before the neutral detergent step for biomasses containing starch. The acid detergent fiber residue (ADF: weight of the acid detergent fiber residue) and the acid detergent lignin (ADL: weight of the acid detergent lignin residue, which is considered as the lignin content) were determined by the VS gravimetric method (Van Soest, 1973) except that, prior to the ADF extraction, an extraction with the neutral detergent without adding sodium sulfite was carried out, as it is done for the NDF. The VS cellulose content was calculated as ADF–ADL. The VS hemicelluloses content was calculated as NDF–ADF (Van Soest and Wine, 1967; Van Soest, 1973). The total soluble sugars were determined by the Luff-Schoorl method (European Union, 2009). The starch content was determined by the Ewers method (European Union, 2009). The protein content was determined by the Kjeldahl method using 6.25 as conversion factor of nitrogen to protein (AOAC, 1990). The mineral content was determined by use of a muffle furnace set at 550 °C for 3 h. The dry matter (DM) content was determined at 103 °C for 4 h.

The monosaccharides xylan, arabinan, mannan, galactan and the total glucan present in the structural polysaccharides were determined on a subset of 255 samples by a sulfuric acid hydrolysis

Table 1
Details about the investigated fibrous biomasses.

	Plant species	Cultivar	Harvest period	Number of samples
Miscanthus giganteus	*Miscanthus* × *giganteus* J.M. Greef & Deuter ex Hodk. & Renvoize	Bical and Tournai	Late winter	74
Miscanthus giganteus	*Miscanthus* × *giganteus* J.M. Greef & Deuter ex Hodk. & Renvoize	Bical	Early autumn	21
Switchgrass	*Panicum virgatum* L.	Alamo, Blackwell, Cave-in-Rock, Dacotah, Kanlow, Nebraska 28, Shelter and Traiblazer	Late winter	128
Switchgrass	*Panicum virgatum* L.	Cave-in-Rock	Early autumn	22
Fiber sorghum	*Sorghum bicolor* (L.) Moench	CA25, ENR10, H133, Maja and Zerberus	Late winter	79
Fiber sorghum	*Sorghum bicolor* (L.) Moench	CA25, ENR10, H133, Maja and Zerberus	Early autumn	53
Spelt straw	*Triticum aestivum* L. ssp. *spelta* (L.) Thell.	Badengold and Cosmos	Late summer	92
"Cocksfoot–alfalfa" mixture	*Dactylis glomerata* L. – *Medicago sativa* L.	Terrano-Europe	3 cycles late spring-late summer-late autumn	27
Tall fescue	*Festuca arundinacea* Schreb.	Hykor, Jordane, Kora, Perun and Soni	3 cycles late spring-late summer-late autumn	175
Immature rye	*Secale cereale* L.	Protector and Vitalio	Early spring	54
Fiber corn	*Zea mays* L.	Athlético, Beethoven, Coryphée, Franky, LG Azelo and Ronaldinio	Late winter	21
Fiber corn	*Zea mays* L.	Aayrton, Athlético, Aventura, Beethoven, Cannavaro, Coryphée, Dominator, Franky, Ladifférence, LG Azelo, Olympus, Ricardinio and Ronaldinio	Early autumn	125
Hemp	*Cannabis sativa* L.	Epsilon 68, Fedora 17 and Futura 75	Early autumn	80
Jerusalem artichoke	*Helianthus tuberosus* L.	Volkenroder spindel	Early autumn	46

method (SAH) after fractionation (Godin et al., 2011). The hemicellulosic glucan content was determined by the SAH method on the same subset of samples except that the cellulose solubilization step (incubation with H_2SO_4 12.2 mol L^{-1} for 1 h at 30 °C) was skipped. The cellulosic glucan content was calculated as the difference between the total glucan and the hemicellulosic glucan content. The Van Soest method is known to overestimates the cellulose and the hemicelluloses content as compared to the SAH method (Lorenz et al., 2009; Wolfrum et al., 2009; Godin et al., 2011). To correct for this bias, the SAH cellulose and the SAH hemicelluloses content of the 999 samples analyzed by the VS method were determined by the relationship between the concentrations of the components determined by the VS and SAH method as based on the dataset developed in our laboratory:

$$\text{Cellulose\_SAH} = (0.844 \times \text{Cellulose\_VS}) + 0.008 \text{ for commelinid monocotyledons biomasses} \times (n = 308,\ R_2 = 0.97,\ \text{RMSE} = 0.014,\ \text{RPD} = 5.9) \quad (1)$$

$$\text{Cellulose\_SAH} = (0.803 \times \text{Cellulose\_VS}) - 0.014 \text{ for non-commelinid dicotyledons biomasses} \times (n = 108,\ R_2 = 0.98,\ \text{RMSE} = 0.021,\ \text{RPD} = 6.4) \quad (2)$$

$$\text{Hemicelluloses\_SAH} = (0.856 \times \text{Hemicelluloses\_VS}) + 0.018 \text{ for commelinid monocotyledons biomasses} \times (n = 308,\ R_2 = 0.85,\ \text{RMSE} = 0.018,\ \text{RPD} = 2.6) \quad (3)$$

$$\text{Hemicelluloses\_SAH} = (1.381 \times \text{Hemicelluloses\_VS}) - 0.008 \text{ for non-commelinid dicotyledons biomasses} \times (n = 108,\ R_2 = 0.88,\ \text{RMSE} = 0.020,\ \text{RPD} = 2.9) \quad (4)$$

The predictions made by a linear regression are considered as reliable when the linear regression has a $R^2 \geq 0.81$ and a RPD ≥ 2.5 (Tamaki and Mazza, 2011).

Cellulose_SAH and hemicelluloses_SAH are mentioned below as cellulose and hemicelluloses, respectively.

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*, 10 min), 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

Table 2
Details about the cropping sites.

Location			Above sea level (m)	Average annual temperature (°C)	Average annual precipitation (mm)
50°33′ N, 04°43′ E	Gembloux	Belgium	161	9.8	856
49°55′ N, 05°24′ E	Libramont	Belgium	498	8.6	1260
50°28′ N, 05°23′ E	Tinlot	Belgium	255	9.7	871
48°29′ N, 06°31′ E	Gerbéviller	France	260	9.9	1022
49°57′ N, 06°33′ E	Mötsch	Germany	330	8.4	675

analyzed by HPLC using an Agilent 1200 series liquid chromatography (LC) system with a quaternary pump (Agilent, Berkshire, UK) connected to a 1200 series Agilent evaporative light scattering detector (ELSD) (Agilent, Berkshire, UK). Nitrogen (0.35 MPa) was used as nebulizer gas. The nebulizer tube temperature was set to 50 °C, and the ELSD gain was set to 9. Samples extracts were diluted (1:20 volume fraction to 1:100 volume fraction) in deionized water with 10% volume percentage of LC-grade acetonitrile were injected (20 μL) and eluted in a Prevail carbohydrates ES analytical LC column (250 mm × 4.6 mm I.D.; 5 μm particle size) (Grace, Lokeren, Belgium) with a Prevail Carbohydrates ES All-guard precolumn (12.5 mm × 4.6 mm I.D.; 5 μm particle size) (Grace, Lokeren, Belgium). The mobile phases consisted of 95:5 (volume fraction) LC-grade acetonitrile:deionized water mixture (A) and 100% deionized water (B). 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 set at 25 °C using an Agilent G1316A thermostated column compartment.

The ELSD response ((peak area) = $a \times$ (concentration)^b, with b set at 1.5) was calibrated for D-glucose, D-fructose, sucrose, raffinose, and stachyose with 5 solutions of the authentic compounds, covering the range of 0.6–3.0 g L^{-1}.

2.3. Biofuel potentials

2.3.1. Enzymatically digestible organic matter

The enzymatically DOM of the biomass, as determined by the De Boever method (De Boever et al., 1986), is used to compare the suitability of the different biomasses to be converted by anaerobic digestion (biomethanation). 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 of the biomass without any pretreatment (De Boever et al., 1986; Lesteur et al., 2011). 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 than the enzyme assay. Briefly, biomass samples were incubated, chronologically, with pepsin in 0.1 mol L^{-1} HCl for 24 h at 40 °C, 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. The solubilization of the biomass was determined gravimetrically.

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 of Spatari et al. (2010), on the basis of (i) the monomers expected from the hydrolysis yields of cellulose, hemicelluloses (hydrolysis yields of respectively 91% and 81% with a liquid hot water pretreatment; da Costa Sousa et al., 2009) and starch (hydrolysis yield of 96%; Buchholz and Seibel, 2008); (ii) the stoechiometric ethanol fermentation yields of monosaccharides (92.5% for glucose and fructose, and 86% for xylose, arabinose, galactose and mannose; Hamelinck et al., 2005) and (iii) the ethanol recovery yield (99.5%; Spatari et al., 2010). The mean relative monosaccharidic content of the hemicelluloses, as presented in Fig. 2(a), was used for calculation. 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.

Table 3
Crop yield (as dry matter) and dry matter content (with its standard deviation) of the investigated biomasses.

Biomass	Crop DM yield (Mg hm^{-2} year^{-1})	Dry matter content (kg kg WM^{-1})
Miscanthus giganteus late winter	12.5	0.789 ± 0.076
Miscanthus giganteus autumn	20.0	0.420 ± 0.043
Switchgrass late winter	6.0	0.839 ± 0.063
Switchgrass autumn	9.0	0.575 ± 0.124
Spelt straw	8.0	0.792 ± 0.094
Fiber sorghum late winter	7.5	0.396 ± 0.081
Fiber sorghum autumn	15.0	0.257 ± 0.047
"Cocksfoot–alfalfa" mixture (3 harvest cycles)	12.0	0.246 ± 0.023
Tall fescue (3 harvest cycles)	12.0	0.253 ± 0.043
Immature rye	3.0	0.214 ± 0.017
Fiber corn late winter	8.0	0.656 ± 0.060
Fiber corn autumn	20.0	0.335 ± 0.032
Hemp	14.0	0.391 ± 0.064
Jerusalem artichoke	11.0	0.292 ± 0.061

2.3.3. Thermal energy

The thermal energy was assessed on the basis of the higher heating value (HHV). The HHV was determined by the method using a Parr controlled oxygen bomb calorimeter (European Committee for Standardization, 2005). The sample was ground, pelletized and dried overnight at 103 °C. The higher calorific value was then measured using a Parr 6200 calorimeter.

2.4. Crop yields

The total harvestable biomass components and expected biofuel yields per hm^2 and per year were determined by multiplying our data with the crop DM yield per hm^2 and per year (Table 3, crop trials made in the area of Gembloux, Belgium; T. Schmit personal communication, unpublished data). The dry matter contents of the harvested biomasses are also shown in Table 3.

2.5. Statistical analysis

The Tukey–Kramer multiple mean comparison test (with $\alpha = 0.05$) based on the ANOVA analysis of these means and the correlation analysis were performed using JMP 7.0.1 (SAS Institute, USA). The starch content was not included because only few biomasses contained starch.

3. Results and discussion

3.1. Biomass chemical composition

The chemical composition of the analyzed biomasses is shown in Fig. 1(a), together with its variability (details shown in Table A1 of the appendix). Ranking of these biomasses by using a Tukey–Kramer multiple mean comparison test performed for the content of each main chemical component is presented in Table A1 of the appendix. Cellulose and hemicelluloses are generally the main chemical components of the DM, except for fiber corn because of its high starch content, and for immature rye and jerusalem artichoke because of their high total soluble sugars contents. The highest lignin and structural carbohydrate contents are offered by late winter miscanthus. The total soluble sugars correspond to the sum of the soluble monosaccharides, sucrose and fructans. The highest total soluble sugars, proteins and mineral compounds content are, respectively, observed in immature

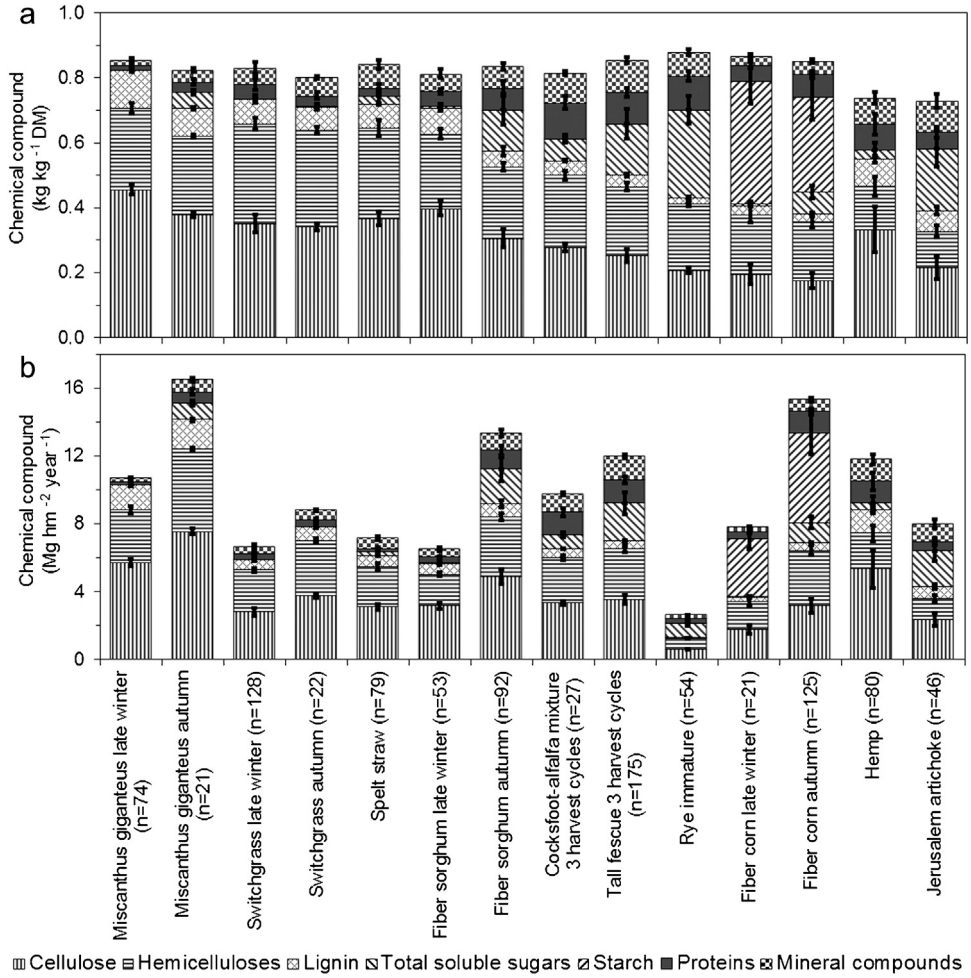

Fig. 1. Main chemical composition (a) and yield (b) of the different investigated biomasses. Error bars correspond to standard deviation, *n* to number of analyzed samples.

rye, "cocksfoot–alfalfa" mixture and tall fescue. Preliminary analyses have shown the absence of starch in all biomasses (data not shown) except fiber corn. Therefore, the starch content has only been determined in the later. Based on the main chemical components, 2 distinctive types of vegetal biomass profiles can be observed in Fig. 1(a) and by the ranking of these biomasses by using a Tukey–Kramer multiple mean comparison test (Table A1 of the appendix):

- Miscanthus, switchgrass, fiber sorghum late winter and spelt straw which have a higher cellulose, hemicelluloses and lignin content, and have a lower non-structural carbohydrates, proteins and mineral compounds content;
- Tall fescue, "cocksfoot–alfalfa" mixture, immature rye, fiber sorghum autumn, fiber corn, hemp and jerusalem artichoke which have a lower cellulose and hemicelluloses content, and have a higher non-structural carbohydrates, proteins and mineral compounds content.

The cleavage between these two groups can be explained by the fact that:

- The biomasses with higher contents of structural components are mainly made of stems with more lignified cell walls (rich in secondary cell walls) that have higher contents of these components to stand up;
- The biomasses with higher contents of non-structural components are mainly made of leaves with much less lignified cell walls and metabolically more active cells.

Fig. 1 shows a 0.12–0.25 kg^{-1} kg_{DM} non-identified fraction in all biomasses. Soluble polysaccharides (such as pectins), acid soluble lignin, organic acids, alcohols, pigments and lipids compose most probably this fraction, as suggested by Hames (2009) for other biomasses. Hemp and jerusalem artichoke have a higher non-identified fraction compared to the other biomasses. This can be explained by their botanical differences. Hemp and jerusalem artichoke are non-commelinid dicotyledons which have a higher pectin and lower hemicelluloses content as compared to the other biomasses that are commelinid monocotyledons. The latter are known to have a lower pectin content and a higher hemicelluloses content (Carpita and McCann, 2000; Godin et al., 2011).

Biomasses harvested in late winter had higher contents of structural components (cellulose, hemicelluloses and lignin) and lower contents non-structural components (total soluble sugars, proteins and mineral compounds) compared to the corresponding biomasses harvested in autumn (Fig. 1(a)). This can be explained by the nutrient translocation to the rhizomes, the solubilization and the leaching of the non-structural components during the winter (Cadoux et al., 2009).

The chemical composition of each analyzed biomass is generally relatively stable independently of crop conditions (small standard deviations in Fig. 1(a) and Table A1 of the appendix). This quite reproducible chemical composition for each type of

Table 4
Cross-correlations between the contents of the biomass main chemical components ($n = 999$).

	Cellulose	Hemicelluloses	Lignin	Total soluble sugars	Proteins	Mineral compounds
Cellulose	–					
Hemicelluloses	0.50***	–				
Lignin	0.89***	0.29***	–			
Total soluble sugars	−0.59***	−0.40***	−0.64***	–		
Proteins	−0.62***	−0.38***	−0.66***	0.53***	–	
Mineral compounds	−0.31***	−0.25***	−0.35***	0.45***	0.61***	–

*** $p < 0.001$.

biomass can be explained by the fact that they have been harvest at the same harvest period. The most variable chemical components are the non-structural carbohydrates (total soluble sugars and starch), and the cellulose content of both hemp and jerusalem artichoke (Fig. 1(a)). For the non-structural carbohydrates, this could be explained by the variability of plant metabolism linked to photosynthesis. For the cellulose content variability of hemp and jerusalem artichoke, this could be explained by their phylogenetic origins.

The significant correlations between the main chemical components are highlighted in Table 4. The correlations between structural components and between non-structural components are all significantly positive. The correlations between structural components and non-structural components are all significantly negative. This can be explained by the distinction underlined above between biomasses mainly made of stems and biomasses mainly made of leaves (Carpita and McCann, 2000).

The biomass chemical components produced per hm^2 and year are summarized in Fig. 1(b). These results are mainly influenced by the crop DM yield. Biomasses harvested in late winter, while presenting higher contents of structural components (cellulose, hemicelluloses and lignin) as discussed above (Fig. 1(a)), have actually lower yields of harvested biomass (Fig. 1). The decrease of biomass yields can be explained by the loss of leaf biomass during the winter (Cadoux et al., 2009). For perennial crops, this decrease in yield can also be explained by the nutrient translocation from the stems and/or leaves to the rhizomes (Cadoux et al., 2009).

An issue for an autumn harvest of miscanthus and switchgrass is that such a harvest disables the crop to translocate its nutrients to its rhizomes (Cadoux et al., 2009). Therefore, to have the same crop yield the following year, it will need a higher fertilization level compared to the same crop harvested in the winter (Cadoux et al., 2009). An increased use of fertilizer will lead to an increase of the amount of greenhouse gas emission due to its out spread and its manufacture (Cadoux et al., 2009).

3.2. Monosaccharidic composition of hemicelluloses

The absolute and relative contents of hemicellulosic components of the analyzed biomasses are shown with their variabilities in Fig. 2(a) and (b), respectively. The absolute contents of hemicellulosic components are also shown in Table A2 of the appendix. Xylan is the major absolute and relative hemicellulosic component. The highest absolute hemicelluloses and xylan contents are found in switchgrass, while the highest relative xylan contents is offered by late winter miscanthus. Based on the hemicellulosic components, 2 distinctive types of vegetal biomass profiles are observed:

- Miscanthus, switchgrass, fiber sorghum, fiber corn, spelt straw, “cocksfoot–alfalfa” mixture, tall fescue and immature rye, where the major relative hemicellulosic components are, by order of decreasing importance, xylan, arabinan, hemicellulosic glucan, galactan and mannan. All these biomasses are commelinid monocotyledons (“cocksfoot–alfalfa” mixture is considered as a commelinid monocotyledon because of the dominance of cocksfoot). Such biomasses are known to have hemicelluloses with higher content of arabinoxylan and β-glucan, as compared to non-commelinid dicotyledons (Carpita and McCann, 2000; Godin et al., 2011);
- Hemp and jerusalem artichoke, where the major relative hemicellulosic components are, by order of decreasing importance, xylan, hemicellulosic glucan, galactan, mannan and arabinan. These biomasses are non-commelinid dicotyledons. Such biomasses are known to have hemicelluloses with higher contents of xyloglucan and mannan, as compared to commelinid monocotyledons (Carpita and McCann, 2000; Godin et al., 2011).

The lower content of arabinan of the analyzed non-commelinid dicotyledons biomasses compared to the analyzed commelinid monocotyledons biomasses confirms that the arabinoxylan of commelinid monocotyledons are more substituted with arabinan, which is known to be highly linked to lignin by ferulate residues (Carpita and McCann, 2000).

The absolute and relative contents of hemicellulosic components showed a low variability within each type of biomass (Fig. 2). These quite reproducible hemicellulosic contents for each type of biomass can be explained by the fact that they have been harvest at the same harvest period.

The correlations between the relative monosaccharidic components of hemicelluloses are highlighted in Table 5. The correlation analysis of the hemicellulosic components was done separately on commelinid monocotyledons and non-commelinid dicotyledons biomasses because of their distinctive hemicelluloses profile, as above mentioned. Hemicelluloses are made of four types of structural polysaccharides: arabinoxylan, xyloglucan (which also contains galactan and hemicellulosic glucan), β-glucan and mannan (which also contains galactan and hemicellulosic glucan) (Ishii, 1997; Vogel, 2008). The high correlation between the relative content of xylan and arabinan in commelinid monocotyledon biomasses (Table 5) 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 compared to more lignified cell walls which have a higher content of arabinoxylan with a lower degree of substitution by arabinan (Ishii, 1997; Carpita and McCann, 2000; Vogel, 2008). This can also explain the high negative correlation between the relative content of xylan and galactan (Table 5), and the high positive correlation between xylan and hemicellulosic glucan in commelinid monocotyledon biomasses (Table 5).

3.3. Soluble and reserve carbohydrates

The mono-, di- and oligo-saccharides that contribute to the total soluble carbohydrates were further characterized for the various biomasses. Fig. 3 presents the total amount of easily fermentable

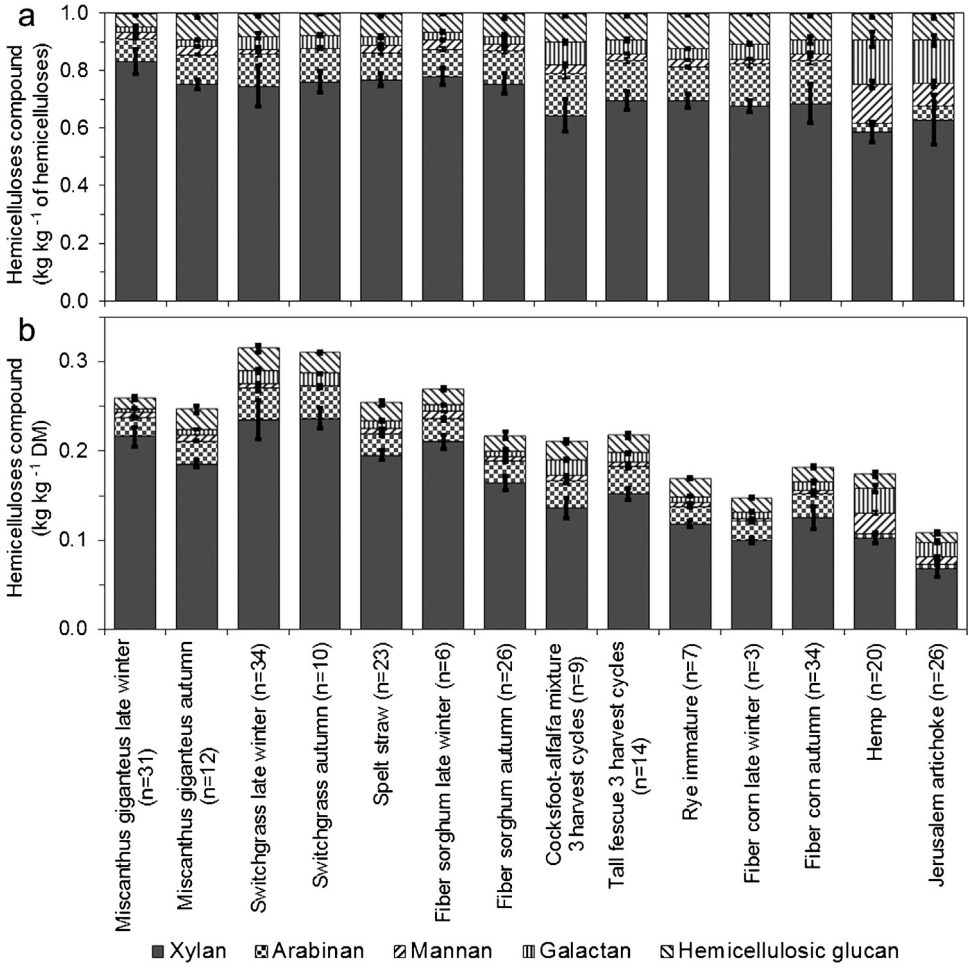

Fig. 2. Relative (a) and absolute (b) monosaccharidic compositions of hemicelluloses of the different investigated biomasses. Error bars correspond to standard deviation, *n* to number of analyzed samples.

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, oligosaccharides up to a degree of polymerization of 25–30 were detected (data not shown). They were considered as oligo-fructans (Downes and Terry, 2010). Oligosaccharides peaks were also detected in the LC chromatograms of autumn fiber sorghum, August cocksfoot–alfalfa and tall fescue.

3.4. Biomass characteristics as guide in the selection of transformation technology

3.4.1. Enzymatically digestible organic matter

The interest of the analyzed biomasses for conversion by anaerobic digestion (biomethanation) was assessed by their contents in enzymatically digestible organic matter (DOM) (Fig. 4). Details of Fig. 4(a) and a ranking of the biomasses after a Tukey–Kramer

Table 5
Cross-correlations between the relative monosaccharidic components of hemicelluloses of the investigated commelinid monocotyledon ($n = 209$) and non-commelinid dicotyledon ($n = 46$) biomasses.

	Xylan	Arabinan	Mannan	Galactan	Hemicellulosic glucan
Commelinid monocotyledons					
Xylan	–				
Arabinan	−0.90***	–			
Mannan	−0.20**	0.02	–		
Galactan	−0.83***	0.76***	−0.04	–	
Hemicellulosic glucan	−0.84***	0.63***	0.07	0.55***	–
Non-commelinid dicotyledons					
Xylan	–				
Arabinan	0.21	–			
Mannan	−0.72***	−0.67***	–		
Galactan	−0.54***	0.10	0.04	–	
Hemicellulosic glucan	−0.08	−0.30*	0.03	−0.38**	–

* $p < 0.050$.
** $p < 0.010$.
*** $p < 0.001$.

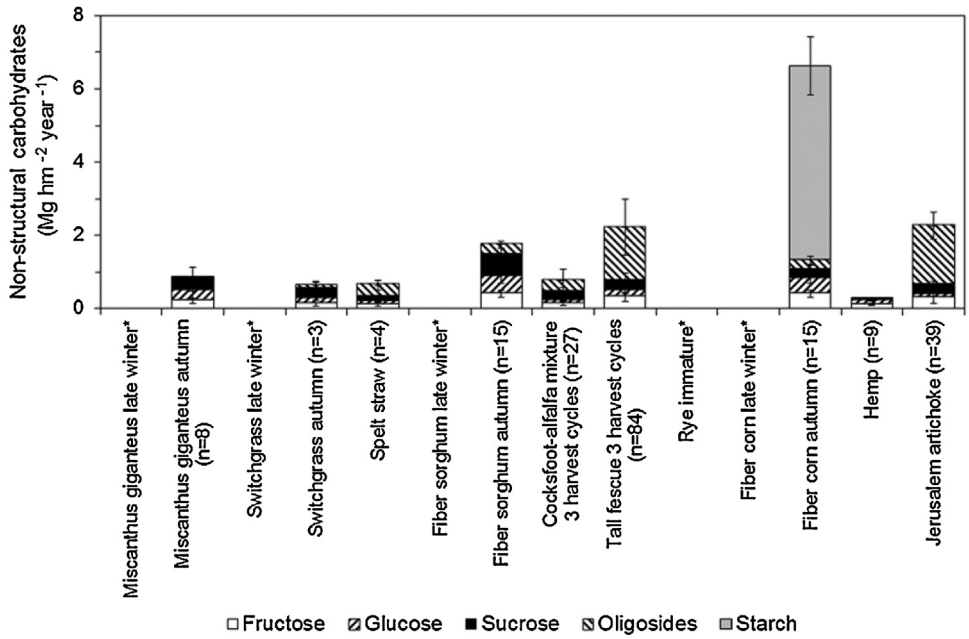

Fig. 3. Identified saccharides that contribute to the total soluble carbohydrates: glucose, fructose, sucrose, other unidentified soluble carbohydrates and starch. Error bars correspond to standard deviation, *n* to number of analyzed samples. *, not determined.

multiple mean comparison test performed for their respective enzymatically DOM are presented in Table A3 of the appendix. 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 (De Boever et al., 1986; De Boever et al., 1988; Lesteur et al., 2011). The biomasses with the highest enzymatically DOM per kg of the dry organic matter are fiber corn and immature rye (Fig. 4(a)).

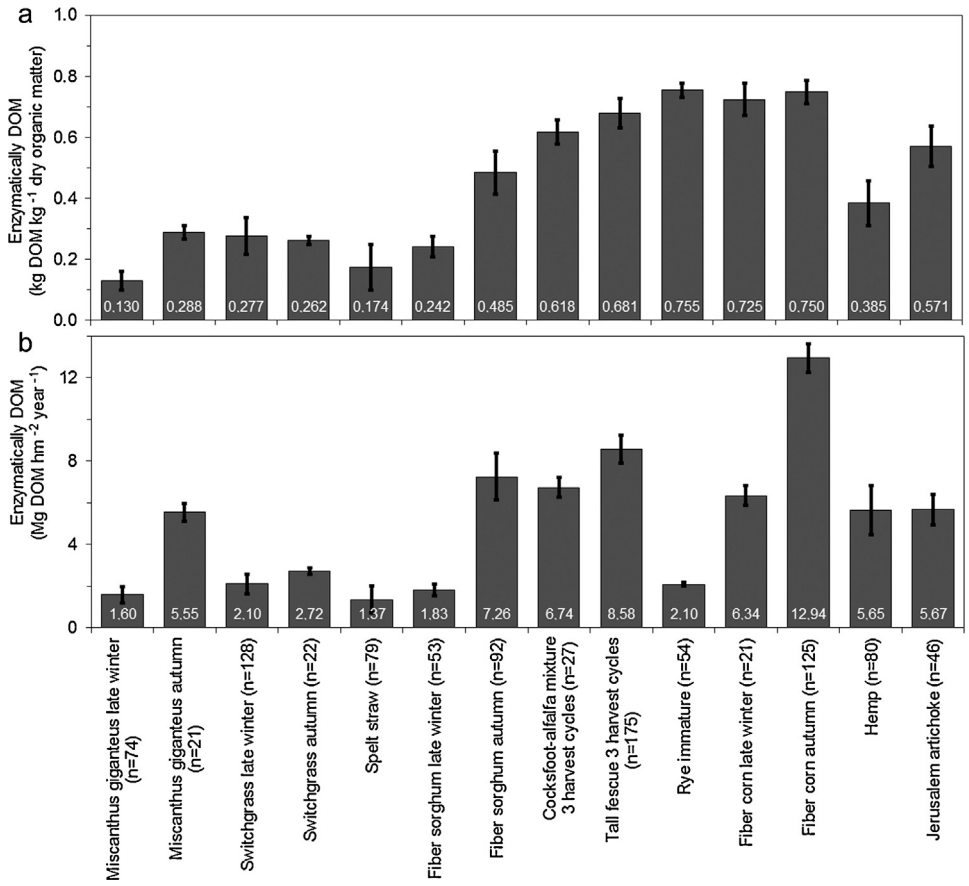

Fig. 4. Enzymatically DOM (a) and yield (b) of the different investigated biomasses. Error bars correspond to standard deviation, *n* to number of analyzed samples.

Table 6
Cross-correlations between enzymatically DOM-bioethanol potential from structural-bioethanol potential from non-structural carbohydrates-higher heating value and the chemical composition of the investigated biomasses ($n = 999$).

	Cellulose	Hemicelluloses	Lignin	Total soluble sugars	Proteins	Mineral compounds
Enzymatically DOM	−0.94***	−0.55***	−0.91***	0.69***	0.74***	0.36***
Bioethanol potential from structural carbohydrates	0.94***	0.77***	0.77***	−0.59***	−0.62***	−0.34***
Bioethanol potential from non-structural carbohydrates	−0.87***	−0.52***	−0.79***	0.50***	0.35***	−0.06
Higher heating value	0.55***	0.53***	0.54***	−0.71***	−0.43***	−0.76***

*** $p < 0.001$.

This can be explained be their high contents of total soluble sugars, starch and/or proteins, which are a part of the enzymatically DOM (De Boever et al., 1986). Crops mainly made of stems, with a high content of (lignified) structural components, have the lowest enzymatically DOM. Crops with an important part of leaves show intermediate enzymatically DOM.

Table 6 presents the correlations between the enzymatically DOM and the main chemical components of the biomass. The enzymatic digestibility is significantly positively and negatively correlated to the non-structural components and structural components, respectively. This can be explained by the enzymatic cocktail used to determine the DOM that is more efficient to hydrolyze the non-structural components.

The enzymatically DOM content showed a low variability within each type of biomass, except for spelt straw (Fig. 4(a)). This low variability can be explained by the low variability observed for the chemical component contents (Fig. 1(a)).

Fig. 4(b) also presents the enzymatically DOM yields that can be harvested per hm^2. The enzymatically DOM yields depend mainly on the biomass DM yield and only to a secondary extent on its digestibility. Biomasses harvested in autumn have a higher enzymatic DOM yield than when harvested in late winter. This can be explained by the higher non-structural content in the autumn harvest.

3.4.2. Bioethanol

Fig. 5 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 need a biomass pretreatment to be fermented. Details of Fig. 5(a) and a biomass ranking after a Tukey–Kramer multiple mean comparison test performed for their respective bioethanol potential are presented in Table A3 of the appendix. The biomasses with highest total bioethanol potential per kg of DM are fiber corn and miscanthus. Late winter miscanthus has the highest ethanol potential based on structural carbohydrates, while fiber corn has the highest ethanol potential based on non-structural carbohydrates. Structural polysaccharides are the main source of potential ethanol for most substrates, exepted fiber

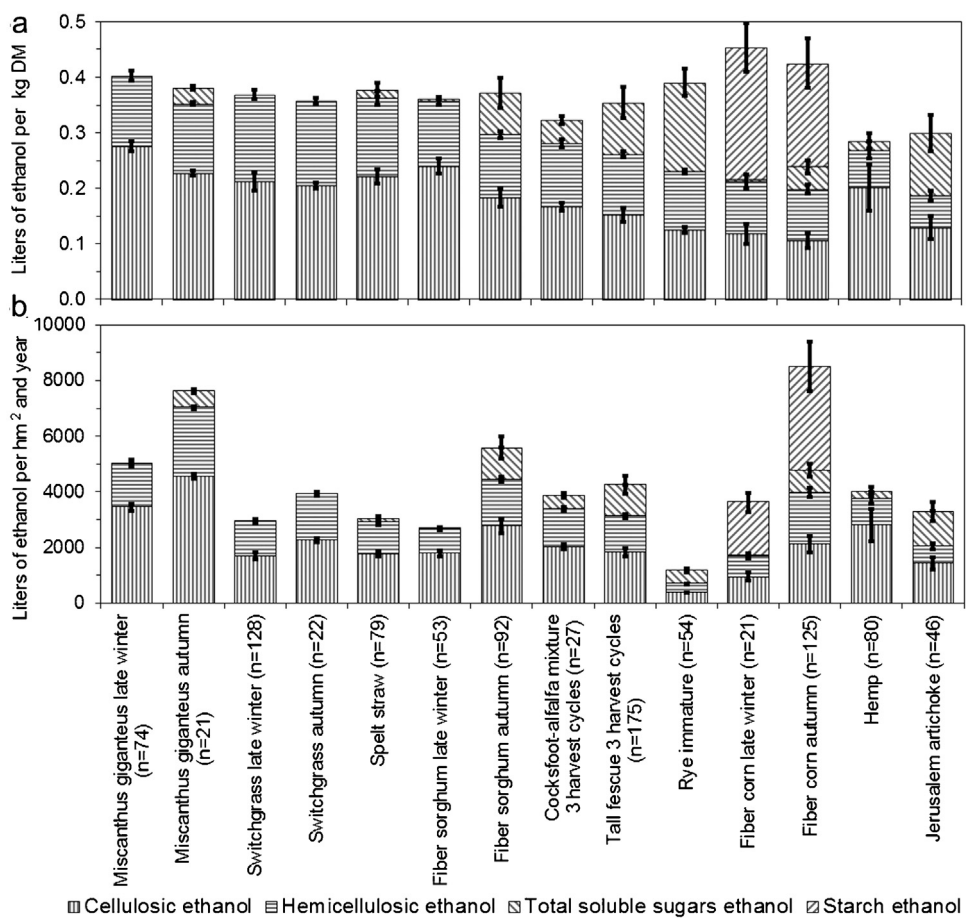

Fig. 5. Potential bioethanol (a) and yield (b) of the different investigated biomasses. Error bars correspond to standard deviation, n to number of analyzed samples.

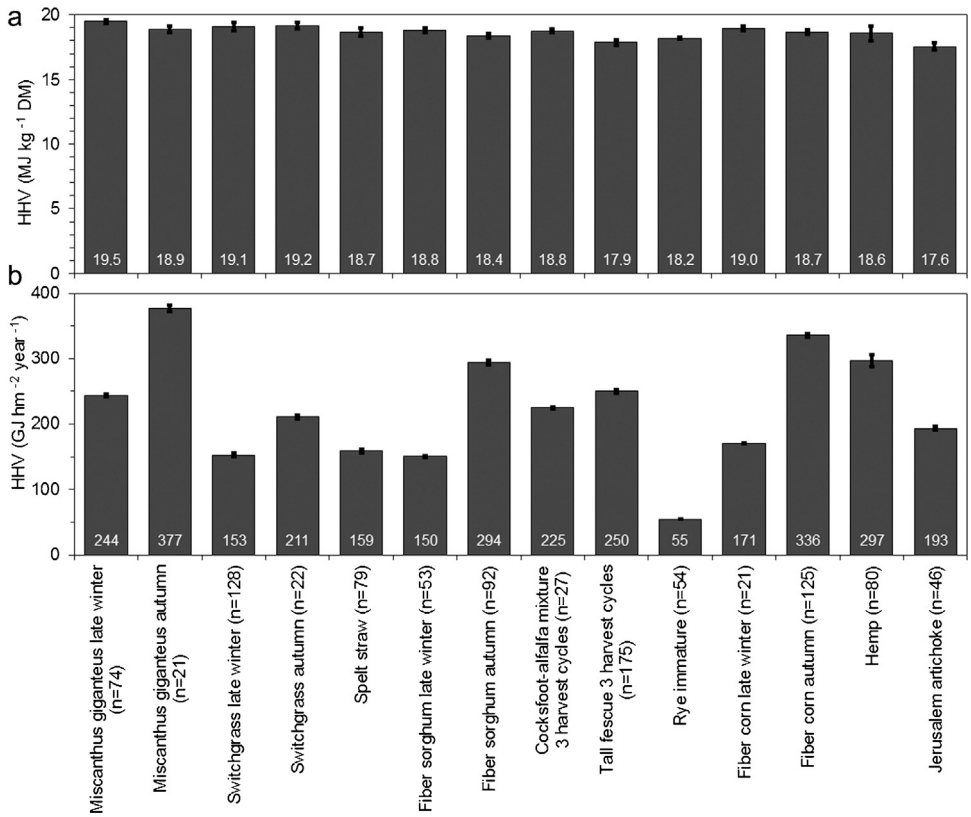

Fig. 6. Higher heating value (a) and yield (b) of the different investigated biomasses of the different investigated biomasses in dry state. Error bars correspond to standard deviation, *n* to number of analyzed samples.

corn, immature rye and jerusalem artichoke, where non-structural carbohydrates bring a significant contribution.

There are highly significant positive and negative correlations between the structural components and, respectively, the bioethanol coming from structural carbohydrates and from non-structural carbohydrates (Table 6), as a direct consequence of the negative correlations of the later discussed in Table 4.

The range of the total bioethanol potential observed for each type of biomass is generally relatively narrow (Fig. 5(a)). This low variability can be explained by the low variability observed for the carbohydrate contents (Fig. 1(a)). The largest variability is observed for biomasses with the highest content of reserve and soluble carbohydrates, in line with the higher variability of the latter with plant metabolism (Fig. 1(a)).

Fig. 5(b) presents the total ethanol production potential that can be expected per hm^2. These results are mainly influenced by the crop DM yield (Table 3). As compared to the autumn harvest, crops harvested in late winter, while presenting higher content of total bioethanol potential per dry mass (Fig. 5(a)), show reduced production per hm^2 due to the loss of harvestable dry matter during winter.

3.4.3. Thermal energy

The potential use of the analyzed biomasses to produce thermal energy by combustion (independently of their humidity that can be adjusted by drying, if required) was assessed by the HHV. Fig. 6 presents the HHV measured for the analyzed biomasses, together with its variability. Details of Fig. 6(a) and ranking of the biomasses after a Tukey–Kramer multiple mean comparison test performed for their respective HHV can be found in Table A3 of the appendix. The biomass with the highest HHV per kg of the DM is the late winter harvested miscanthus. The highest significant correlation between the HHV and the main chemical components is the one with the mineral compounds content ($r = -0.76$; $p < 0.001$) (Table 6). This can be explained by the influence of the total organic matter content (complement of the mineral compounds) on the HHV, the relatively low contents of lignin (HHV 25.10 MJ kg^{-1} dry lignin; Klass, 2004) and of proteins (HHV 24.00 MJ kg^{-1} dry protein; Klass, 2004), and the relatively low differences of HHV between the other individual organic compounds (monosaccharides 15.60 MJ kg^{-1} dry monosaccharide; polysaccharides 17.50 MJ kg^{-1} dry polysaccharide; Klass, 2004). The HHV is negatively correlated with the enzymatically DOM ($r = -0.58$; $p < 0.001$) (Table 7). This can be explained by the fact that biomasses with high HHV have an organic matter with higher lignin content which is a highly enzymatically indigestible organic matter and has a high HHV. Biomasses with low HHV have an organic matter with lower lignin content but with higher contents of other organic components that are more enzymatically DOM and have a lower HHV.

The range of HHV observed for each analyzed biomass is very narrow (Fig. 6(a)). This can be explained by the fact that the HHV is related to the mineral compounds (complement of the organic matter content) for which a very narrow range is also observed (Fig. 1(a)).

Fig. 6(b) presents the total thermal energy that can potentially be produced by combustion of the biomass that can be harvested per hm^2, considering that the biomass is available in dry state. As for the other potential valorizations, HHV per hm^2 depends more on the yield of DM per hm^2 than on biomass composition. As for the other energy potentials, loss of harvestable biomass during the winter has a negative impact on the potential that can be recovered after winter. An efficient conversion of vegetal biomass to thermal energy by combustion requires that the biomass has a high DM content

Table 7
Cross-correlations between the enzymatically DOM, bioethanol potential from structural carbohydrates, bioethanol from non-structural carbohydrates and higher heating value of the investigated biomasses ($n = 999$).

	Enzymatically DOM	Bioethanol potential from structural carbohydrates	Bioethanol potential from non-structural carbohydrates	Higher heating value
Enzymatically DOM	–			
Bioethanol potential from structural carbohydrates	−0.91***	–		
Bioethanol potential from non-structural carbohydrates	0.84***	−0.85***	–	
Higher heating value	−0.58***	0.63***	−0.37***	–

*** $p < 0.001$.

and a low mineral compounds content. Indeed, the water content of biomass induces a loss of energy and the mineral compounds produces clinkers. The winter harvest has a higher DM content and lower mineral compounds content compared to the autumn harvest (Fig. 1(a) and Table 3). This is the case of the winter harvest and the spelt straw.

4. Conclusions

Analyzed biomasses show 2 distinctive patterns: either a high content of structural components with low content of non-structural components, or the opposite. The relative hemicellulosic components profile shows 2 distinctive patterns according to plant groups: (i) commelinid monocotyledons with, by order of decreasing importance, xylan, arabinan, hemicellulosic glucan, galactan and mannan; (ii) non-commelinid dicotyledons with, by order of decreasing importance, xylan, hemicellulosic glucan, galactan, mannan and arabinan.

The composition of each type of biomass remained relatively constant despite the diversity of the cropping and harvest conditions (year, area, cultivar and nitrogen fertilization level). Consistently, the measured enzymatically DOM, the calculated bioethanol potential and the measured higher heating values were also quite reproducible for the analyzed biomass. Based on the biomass composition, fiber corn, immature rye and tall fescue appear as the best substrates for anaerobic digestion (low cellulose and lignin contents); late winter harvested miscanthus is the best substrate for combustion (high organic matter and low water contents); fiber corn and late winter harvested miscanthus are also the best substrates for bioethanol production (high total carbohydrates content as cellulose, hemicelluloses and starch).

Fiber corn harvested in autumn offers the highest potential for both digestible organic matter and total bioethanol, owing to its high dry biomass yield, high structural carbohydrates and starch contents and high digestibility. Both fiber corn and miscanthus harvested in autumn offer the highest energy yields per unit area (hm^2) (as higher heating values), owing to their significantly higher dry biomass yield as compared to the other crops. In all cases, autumn harvest offers better yields than late winter harvest, mainly due to a loss of harvestable biomass during winter, and not significantly due to the evolution of their composition.

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 no. 14GR23024 of the European Territorial Co-operation Program in the context of INTERREG IV A «Grande Région» 2007–2013 no. 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.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.indcrop.2013.04.007.

References

AOAC, 1990. Official Methods of Analysis, 15th ed. Association of Official Analytical Chemist, Washington, DC.
Bessou, C., Ferchaud, F., Gabrielle, B., Mary, B., 2011. Biofuels, greenhouse gases and climate change. A review. Agron. Sustainable Dev. 31, 1–79.
Buchholz, K., Seibel, J., 2008. Industrial carbohydrate biotransformations. Carbohydr. Res. 343, 1966–1979.
Cadoux, S., Briand, S., Chabbert, B., Besnard, A., Félix, I., Savouré, M., Marsac, S., Preudhomme, M., Labalette, F., Boizard, H., 2010. Biomass productivity of different energy crops under French conditions: results of the Regix experimental network. In: 18th European Biomass Conference & Exhibition, Lyon.
Cadoux, S., Preudhomme, M., Machet, J., Mary, B., Fourdinier, E., Ferchaud, F., Boizard, H., Gosse, G., 2009. Productivity and environmental impacts of energy crops first results of the long term experiment «biomass & environment». In: 17th European Biomass Conference & Exhibition, Hamburg.
Carpita, N., McCann, M., 2000. The cell wall. In: Buchanan, B., Gruissem, W., Jones, R. (Eds.), Biochemistry and Molecular Biology of Plants. American Society of Plant Physiologists, Rockville, pp. 52–108.
Chandel, A., Singh, O., Rao, L., 2010. Biotechnological applications of hemicellulosic derived sugars: state-of-the-art. In: Singh, O., Harvey, S. (Eds.), Sustainable Biotechnology: Sources of Renewable Energy. Springer, New York, pp. 63–81.
Commission of the European Communities, 2003. Directive 2003/30/CE of the European parliament and of the council of 8 May 2003 on the promotion of the use of biofuels or other renewable fuels for transport. Off. J. Eur. Union L123, 42–46.
da Costa Sousa, L., Chundawat, S., Balan, V., Dale, B., 2009. 'Cradle-to-grave' assessment of existing lignocellulose pretreatment technologies. Curr. Opin. Plant Biol. 20, 1–9.
De Boever, J., Cottyn, B., Andries, J., Buysse, F., Vanacker, J., 1988. The use of a cellulase technique to predict digestibility, metabolizable and net energy of forages. Anim. Feed Sci. Technol. 19, 247–260.
De Boever, J., Cottyn, B., Buysse, F., Vanacker, J., 1986. The use of an enzymatic technique to predict digestibility, metabolisable and net energy of compound feedstuffs for ruminants. Anim. Feed Sci. Technol. 14, 203–214.
Downes, K., Terry, L., 2010. A new acetonitrile-free mobile phase method for LC–ELSD quantification of fructooligosaccharides in onion (*Allium cepa* L.). Talanta 82, 118–124.
ENERBIOM, 2012. ENERBIOM: Rapport final de projet. Province de Liège – Services agricoles, Waremme.
European Committee for Standardization, 2005. CEN/TS 14918: Solid Biofuels – Method for the Determination of Calorific Value. European Committee for Standardization, Brussels.
European Union, 2009. Commission Regulation No 152/2009. Off. J. Eur. Union L54, 1–130.
Ghysel, F., Godin, B., Flamin, C., Delfosse, P., Delcarte, J., Stilmant, D., 2010. Valorisation énergétique des fourrages: comparaison de trois filières, enjeux et opportunités. Fourrages 203, 163–173.
Godin, B., Agneessens, R., Gerin, P., Delcarte, J., 2011. Composition of structural carbohydrates in biomass: precision of a liquid chromatography method using a neutral detergent extraction and a charged aerosol detector. Talanta 85, 2014–2026.
Godin, B., Agneessens, R., Gofflot, S., Lamaudière, S., Sinnaeve, G., Gerin, P., Delcarte, J., 2010. Détermination de la cellulose, des hémicelluloses, de la lignine et des cendres dans diverses cultures lignocellulosiques dédiées à la production de bioéthanol de deuxième génération. Biotechnol. Agron. Soc. Environ. 14, 549–560.
Hamelinck, C., van Hooijdonk, G., Faaij, A., 2005. Ethanol from lignocellulosic biomass: techno-economic performance in short-middle- and long-term. Biomass Bioenergy 28, 384–410.

Hames, B., 2009. Biomass compositional analysis for energy applications. In: Mielenz, J. (Ed.), Biofuels: Methods and Protocols. Methods in Molecular Biology, vol. 581. Humana Press, New York, pp. 145–183.
Ishii, T., 1997. Structure and functions of feruloylated polysaccahrides. Plant Sci. 127, 111–127.
Kamm, B., Kamm, M., 2004. Principles of biorefineries. Appl. Microbiol. Biotechnol. 64, 137–145.
Klass, D., 2004. Biomass for renewable energy and fuels. Encyclopedia Energy 1, 193–212.
Lesteur, M., Latrille, E., Maurel, V., Roger, J., Gonzalez, C., Junqua, G., Steyer, J., 2011. First step towards a fast analytical method for the determination of biochemical methane potential of solid wastes by near infrared spectroscopy. Bioresour. Technol. 102 (3), 2280–2288.
Lorenz, A., Coors, J., de Leon, N., Wolfrum, E., Hames, B., Sluiter, A., Weimer, P., 2009. Characterization, genetic variation, and combining ability of maize traits relevant to the production of cellulosic ethanol. Crop Sci. 49, 85–98.
McKendry, P., 2002. Energy production from biomass (part 1): overview of biomass. Bioresour. Technol. 83, 37–46.
Pauly, M., Keegstra, K., 2008. Cell-wall carbohydrates and their modification as a resource for biofuels. Plant J. 54, 559–568.
Spatari, S., Bagley, D., MacLean, H., 2010. Life cycle evaluation of emerging lignocellulosic ethanol conversion technologies. Bioresour. Technol. 101, 654–667.
Tamaki, Y., Mazza, G., 2011. Rapid determination of lignin content of straw using fourier transform mid-infrared spectroscopy. J. Agric. Food Chem. 59, 504–512.
Van Soest, P., Wine, R., 1967. Use of detergents in the analysis of fibrous feeds. IV. Determination of plant cell-wall constituents. J. Assoc. Off. Anal. Chem. 50 (1), 50–55.
Van Soest, P., 1973. Collaborative study of acid-detergent fiber and lignin. J. Assoc. Off. Anal. Chem. 56 (4), 781–784.
Vogel, J., 2008. Unique aspects of the grass cell wall. Curr. Opin. Plant Biol. 11, 301–307.
Wolfrum, E., Lorenz, A., de Leon, N., 2009. Correlating detergent fiber analysis and dietary fiber analysis data for corn stover collected by NIRS. Cellulose 16, 577–585.