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Characterisation of Italian and Dutch forestry and agricultural residues for the applicability in the bio-based sector

Italo Pisanó[a,b,*], Lalitha Gottumukkala[b], Daniel J. Hayes[b], James J. Leahy[a]

[a] *Department of Chemical Sciences, School of Natural Sciences, University of Limerick, Ireland*
[b] *Celignis Limited, Unit 11 Holland Road, Plassey Technology Park, Castletroy, Co. Limerick, Ireland*

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ABSTRACT

Knowing the accurate composition of biomass is of crucial importance in order to assess and decide on the use and processes to be applied to specific biomass types. In this study, the composition of the lignocellulosic constituents present in forestry, agricultural and underutilised waste residues was assessed. Considering the increased interest on hemicellulose fractions for application in biomaterials and biomolecules, large emphasis has been given in detailing the monomeric constituents of the hemicellulose polymer. Lignin and cellulose, the two other major components of lignocellulosic biomass, were analysed and correlated with the trends in the other constituents.

In the samples analysed, the total structural sugars content ranged from 26.0 to 67.5% of the biomass dry weight, indicating high variation between different feedstock and fractions. Hemicellulose concentration and composition also varied significantly (from 38.8% in birch (*Betula Pendula Roth*) foliage to 22.0 % in rice (*Oryza sativa* L.) straw) between the feedstock types and within the same feedstock type between different species and different fractions. The extractives content varied greatly between the different species (from 2.66 % to 30.47 % of the biomass dry weight) with high contents in certain fractions of feedstock suggesting more detailed compositional analysis of these extracts is warranted.

1. Introduction

Lignocellulosic biomass constitutes of cellulose, hemicellulose, the polymer lignin and other non-structural components such as extractives (Mansor et al., 2019). Though the constituents are the same, the composition of the sugars varies between plant species and some of this variation can be attributed to the hemicellulose constituents (Schädel et al., 2010).

Cellulose is widely tested for a variety of applications and recently the focus is shifting towards its potential as biopolymer in bioplastics and biomedical sector (Klemm et al., 2005). Hemicellulose is generally regarded as an obstacle to access cellulose, however recently hemicellulose has gained attention as a polymer for bio-based materials production. Hemicellulose is generally regarded as an obstacle to access cellulose, however recently hemicellulose has gained attention as a polymer for bio-based materials production, but its potential is not fully studied due to its complex nature. Unlike cellulose, hemicellulose composition varies greatly between the species and plant fractions, according to the plant species and the distribution of the cells within the plant itself and constitute approximately between 20 % and 40 % of the plant cell walls on dry basis. However, in certain annual plants they are present even in higher concentrations, becoming an enormous resource for the production of bio-based materials (Tarasov et al., 2018).

Lignin is another highly abundant organic polymer, and its main role is to fill the space between the cell membranes of plants and provide strength and rigidity to the plant. The percentage of lignin varies widely between plants species and across the age of the plants. The application potential of lignin is enormous and is widely tested for heat insulation, to produce resins and coatings, nutritional supplements, foams, surfactants, films, paints, and in several plastics (Vertichem Corp, 2008).

Though the technology for producing biofuels (e.g. bioethanol, biodiesel) and bio-based products from lignocellulosic sources is advancing rapidly in order to meet demand and chemical needs, the variability of lignocellulosic biomass composition across different feedstock is not well documented (Wang and Howard, 2017). The importance of determining the concentration of the major constituents in biomass samples is crucial since it is usually directly proportional to the yields of products obtained from them. For example, the hemicellulose-lignin ratio is a

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* Corresponding author at: Department of Chemical Sciences, School of Natural Sciences, University of Limerick, Ireland.
E-mail address: italo.pisano@ul.ie (I. Pisanó).

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good predictor of digestibility of biomass and the enzyme requirements, which are two essential parameters for the production of biofuels and bio-based products (Adams et al., 2018). Nevertheless, it is also important to assess the minor constituents (e.g. ash, organic acids, elements) in relation to the running of an industrial-scale biorefinery and the issues that might be encountered with the presence of certain minor constituents (e.g. degradation of metal in process reactors) (Sluiter et al., 2010). In addition to the above, another important fraction of plant biomass are extractives. Extractives are non-structural components of biomass, which are generally minerals and secondary metabolites of plants that are produced mostly as defence strategy. Hence, they are considered a rich source of bioactives (Anouhe et al., 2018). Though there are several publications on bioactive molecules from various plant species, the complex and variable composition of forestry and agricultural extracts does not allow for easy and rapid exploitation. Therefore, the most appropriate analytical protocols for characterizing these type of extracts must be considered before deploying production strategies. (Barbini et al., 2020).

The purpose of the current study is to determine the concentration of major and minor chemical constituents present in forestry (birch (*Betula Pendula Roth*), beech (*Fagus Sylvatica* L.), poplar *(Populus Tremula* L.), olive (*Olea Europaea* L.)) and agriculture (corn stover (*Zea Mays* L.), wheat straw (*Triticum* L.), rice straw (*Oryza sativa* L.), sunflower straw (*Helianthus Annuus* L.), roadside grass (*Heteropogon contortus* L.), cocoa pod husk (*Theobroma Cacao* L.), cow (*Bos Taurus* L.) manure, switchgrass (*Panicum Virgatum* L.)) biomass in order to obtain information on how the selected feedstock could fit into an industrial-scale biotransformation process and their efficient use in terms of obtaining bio-based final products, from fuels to biopolymers and biochemicals. This work includes a comprehensive set of data on a wide range of feedstock and different species within the feedstock (wood, bark, branches and foliage). The research focuses on forestry feedstock harvested mainly in Northern Europe and straws harvested in Italy. Other agriculture residues (e.g. corn stover, cocoa pod husks), farm residues (e.g. cow manure fibres) and grasses were also assessed to broaden the scope and the availability of biomass sources within the European area.

The samples utilised in this research were obtained during the involvement in the BBI-JU Horizon 2020 project UNRAVEL, which focus on the development of advanced pre-treatment, separation and conversion technologies for lignocellulosic biomass in order to obtain recoverable lignin fractions and monomeric sugars from the cellulose and hemicellulose constituents. One of the technologies developed for the project was the FABIOLA$^{\text{TM}}$ [1] fractionation process, which uses low-temperature aqueous acetone to achieve the fractionation of the main lignocellulosic constituents. This technology was previously tested for wheat straw, corn stover, birch, beech and poplar (Smit and Huijgen, 2017). Only hardwoods, straws and grasses were tested in our study, due to the relatively low rates of delignification associated with softwoods under the mild pretreatment conditions (Nitsos et al., 2018). The most common examples of lignocellulosic biomass materials considered sources for the production of biofuel and other bio-based materials include crop residues (e.g. corn stover and wheat straw), hardwood residues (forestry) and seasonal grasses (e.g. switchgrass, roadside grass) (Sluiter et al., 2010).

2. Materials and methods

2.1. Forestry and agricultural biomass

Forestry and agricultural residue biomass were sourced from nine different species, which were sub-divided further as follows (25 samples):

- Forestry Residues:
  1. Birch (*Betula Pendula Roth*): 1) debarked birch chips, 2) debarked birch stem wood chips, 3) birch bark, 4) birch foliage, 5) birch branches, 6) birch whole stem wood chips (including the bark);
  2. Olive Tree (*Olea Europaea* L.): 7) olive tree residue, 8) intact olive branches
  3. Poplar (*Populus Tremula* L.): 9) debarked poplar wood chips, 10) poplar bark, 11) poplar foliage, 12) poplar branches
  4. Beech (*Fagus Sylvatica* L.): 13) debarked beech wood chip, 14) beech bark, 15) beech foliage, 16) beech branches
- Agricultural Residues:
  1. Grass: 17) Switchgrass (*Panicum Virgatum* L.), 18) Roadside Grass (*Heteropogon contortus* L.)
  2. Straw: 19) rice straw (*Oryza sativa* L.), 20) wheat straw (*Triticum* L.), 21) sunflower straw (*Helianthus Annuus* L.), 22) rapeseed straw (*Brassica Napus* L.)
  3. Corn Stover Residues (Maize Stover Residues) (*Zea Mays* L.) (23)
  4. Cow (*Bos Taurus* L.) Manure Fibres (24)
  5. Cocoa Pod Husks (*Theobroma Cacao* L.) (25)

Olive trees and straws were provided by ITABIA (Italian Biomass Association) and were harvested in the Marche region, in central Italy. The remaining samples were provided by TNO and were harvested from across several areas in the Netherlands.

2.2. Extraction procedure

Extractions were carried out with a Dionex Accelerated Solvent Extractor (ASE) 200. Four different extractions were performed: WE (water extraction) where deionised water was used as solvent; EE (ethanol extraction) where 95 % ethanol was used as solvent; FE (full/sequential extraction) where deionised water extraction was followed by ethanol 95 % extraction; and AE (acetone extraction) where 95 % acetone was used as solvent. The extractions were carried out according to the National Renewable Energy Laboratory (NREL) standard operating procedure for the determination of extractives in biomass (Sluiter et al., 2008b).

2.3. Moisture content

Moisture content was assessed by measuring the mass loss from a sample weighing 250 ± 50 g after drying for 18–20 h at 105°C in an oven.

Moisture content was determined according to EN 14774-1:2009.

2.4. Ash

Ash content was determined using a Nabertherm L-240H1SN furnace, according to the NREL operating procedure for the determination of ash in biomass (Sluiter et al., 2008a).

2.5. Hydrolysis of extractives-free samples

Hydrolysis of the dry extractives-free samples was performed according to Hayes modification of the NREL standard operating procedure for the determination of structural carbohydrates and lignin in biomass (Hayes, 2012).

The procedure was divided in two main steps: a two-stage acid hydrolysis of the samples and the gravimetric filtration of the hydrolysate in order to separate it from acid-insoluble residue (AIR) (Sluiter et al., 2008c).

2.6. Lignocellulosic sugars and lignin

The procedure for the determination of lignin and lignocellulosic sugars is summarised:

1) Klason lignin was calculated by determining the weight difference between the AIR and its ash content (CELIGNIS, 2020).
2) Acid soluble lignin was measured by determining the absorbance of an aliquot of the hydrolysate at 240 nm using an Agilent 8452 UV–vis spectrophotometer. The results are then converted to ASL based on Beer's law (Bhagia et al., 2016).
3) The lignocellulosic sugars resulting from hydrolysis were determined by ion-chromatography techniques adapted from Hayes, 2012. The method consisted in diluting the hydrolysate samples 20× with a deionized water solution containing known amounts of melibiose as an internal standard. The diluted hydrolysates were filtered using 0.2 µm Teflon syringe filters and stored in 1.5 ml vials. The vials were then placed into a Dionex ICS-3000 AS50 auto-sampler. The chromatography system also consists of an electrochemical detector (PAD), a gradient pump, a temperature controlled column and a detector compartment. The AS50 injected 10 µl of the diluted sample and the sugar separation (arabinose, rhamnose, galactose, glucose, xylose, and mannose, followed by the internal standard melibiose) was achieved in 35 min through a Carbo-Pac PA1 guard and analytical column, connected in series. Deionised water was used as the eluent; the flow rate was 1.1 mL/min; the column/detector temperature was 21 °C. The PAD detector requires alkaline conditions to detect carbohydrates; therefore, NaOH (300 mM) was added to the post-column flow with a rate of 0.3 mL/min, using a Dionex GP40 pump (Hayes, 2012).

2.7. *Uronic acids and acetyl content*

1) The uronic acids present in the samples were determined by employing a ramping program consisting of sodium acetate and sodium hydroxide gradient, in order to separate the uronic acids (4-*O*-methyl-D-glucuronic acid, galacturonic acid, and glucuronic acid) (Basumallick and Rohrer, 2017). The program was deployed after 35 min following the sugars determination program described above (Hayes, 2012).
2) Acetyl content in the hydrolysates was determined using the Dionex ICS-3000 HPLC-UV with spectra collection at 210 nm. The guard and columns used were a Dionex Acclaim organic acid guard and analytical columns, with operating temperature of 30 °C and isocratic flow of 100 mM of Na_2SO_4 at 0.8 mL/min (Hayes, 2018).

2.8. *Elemental analysis*

Carbon, hydrogen, and nitrogen contents of the samples were determined using an Elementar Macro cube via combustion of the samples at 1150 °C and detection of the gases by thermal conductivity detector (Hayes, 2018).

The sulphur content was determined via ion chromatography analysis (using conductivity detection) of washings of a bomb calorimeter, in accordance with EN15289-2011.

The oxygen content was determined by the difference required to make a mass closure of 100 % when considering the sum of the carbon, hydrogen, nitrogen, sulphur and ash contents.

All the analyses were undertaken in duplicate and the standard deviation between the replicates was determined and presented below.

3. Results

3.1. *Moisture and ash content*

The moisture content of the samples in their 'as received state' (samples analysed the way they were received by Celignis laboratories) are summarised in Table 1. Results showed values ranging from 3.92 % (processed cow manure) to 65.81 % (beech foliage), on a wet mass basis. In terms of ash content, on % dry mass, the biomass derived from forestry sector had low ash with wood samples being the lowest (<1 %), followed by branches (<3 %) and foliage (<5 %). The agricultural residue straw samples had relatively high ash contents, ranging from 6.22 % (rapeseed straw) to 15.82 % (rice straw). Switchgrass, an energy crop, had relatively low ash (3.59 %) compared with roadside grass (12.44 %). The concentrations of ash are crucially important to assess the risk of wear of biomass processing equipment, as ash is believed to have strong abrasive properties. Forestry and agricultural biomass contains ash as a result of normal physiological processes. However, ash contents in

Table 1

Moisture content of different forestry and agriculture feedstock (included residues and waste) for dry matter state and on as received basis.

	Dry Matter Basis (% Dry Mass)				As Received Basis (% Wet Mass)							
	Ash				Moisture Content				Ash			
Sample Name	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*
Beech Bark	4.24	4.24	4.24	*0.00*	43.13	42.96	43.31	*0.25*	2.41	2.41	2.41	*0.00*
Beech Branches	1.93	1.90	1.96	*0.05*	41.17	41.33	41.01	*0.23*	1.14	1.12	1.16	*0.03*
Beech Foliage	5.21	5.20	5.21	*0.01*	65.81	66.01	65.60	*0.29*	1.78	1.78	1.78	*0.00*
Beech Stemwood	0.57	0.59	0.56	*0.02*	46.38	46.31	46.45	*0.09*	0.31	0.32	0.30	*0.01*
Birch Bark	2.26	2.24	2.27	*0.02*	41.63	41.62	41.63	*0.00*	1.32	1.31	1.33	*0.01*
Birch Branches	1.66	1.67	1.64	*0.02*	41.55	41.68	41.42	*0.19*	0.97	0.98	0.96	*0.01*
Birch Foliage	4.60	4.58	4.62	*0.03*	60.20	60.40	60.00	*0.28*	1.83	1.82	1.84	*0.01*
Birch Stemwood	0.40	0.38	0.41	*0.02*	45.13	44.84	45.42	*0.41*	0.22	0.21	0.23	*0.01*
Birch Wood + Bark	1.31	1.29	1.33	*0.03*	4.76	4.58	4.94	*0.25*	1.24	1.22	1.26	*0.03*
Cocoa Pod Husk	10.10	10.25	9.95	*0.21*	14.14	14.17	14.12	*0.03*	8.67	8.80	8.54	*0.18*
Corn Stover	7.05	6.96	7.15	*0.13*	11.92	11.99	11.84	*0.11*	6.21	6.13	6.29	*0.12*
Cow Manure	12.51	12.55	12.47	*0.06*	3.92	4.04	3.80	*0.17*	12.02	12.06	11.98	*0.06*
Olive Tree	1.26	1.28	1.24	*0.03*	31.76	31.71	31.81	*0.07*	0.86	0.87	0.85	*0.02*
Poplar Bark	3.04	3.09	2.98	*0.08*	50.36	50.53	50.20	*0.23*	1.51	1.54	1.48	*0.04*
Poplar Branches	2.25	2.28	2.22	*0.04*	42.34	42.34	42.33	*0.01*	1.30	1.31	1.28	*0.03*
Poplar Foliage	5.21	5.23	5.19	*0.02*	54.69	54.80	54.58	*0.16*	2.36	2.37	2.35	*0.01*
Poplar Stemwood	0.48	0.48	0.48	*0.00*	50.64	50.72	50.55	*0.12*	0.24	0.24	0.24	*0.00*
Rapeseed Straw	6.22	6.21	6.24	*0.03*	13.08	13.19	12.96	*0.17*	5.41	5.39	5.42	*0.02*
Rice Straw	15.82	15.84	15.80	*0.03*	8.39	8.36	8.42	*0.05*	14.49	14.51	14.47	*0.02*
Road Side Grass	12.44	12.56	12.32	*0.17*	11.49	11.51	11.47	*0.03*	11.01	11.12	10.90	*0.15*
SAPPI Birch Chips	0.23	0.21	0.25	*0.03*	28.78	29.73	27.84	*1.34*	0.17	0.15	0.18	*0.02*
Sunflower Straw	9.86	9.85	9.87	*0.02*	12.28	12.31	12.24	*0.04*	8.65	8.64	8.66	*0.02*
Switchgrass	3.59	3.58	3.60	*0.02*	7.30	7.50	7.09	*0.29*	3.33	3.32	3.34	*0.02*
Wheat Straw	7.55	7.54	7.56	*0.02*	9.76	9.69	9.83	*0.10*	6.81	6.80	6.82	*0.02*[a]

[a] AV – Average, R1 – Replicate 1, R2 – Replicate 2, SD – Standard Deviation.

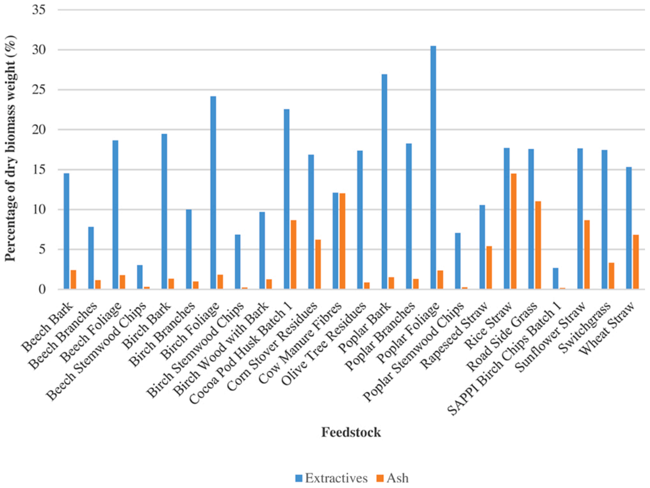

Fig. 1. *Extractives and Ash Concentrations.* Full extractives and ash trends in the feedstock.

harvested biomass can also be incorporated by soil and dust during harvesting and collection (Lacey et al., 2018). The process residue feedstock tested in this study were cocoa pod husks and fibre rich fraction of cow manure and they showed ash values similar to the ash values of the straws (>10 %). Ash contents were also correlated with extractives contents (Fig. 1). For more details, see Table 1.

3.2. *Total structural sugars, hexosans and pentosans*

The total structural sugars (sum of hexosans and pentosans) content varied from 26.02 % (cocoa pod husk) up to 67.46 % (Birch Chips) of the dry biomass (Table 2). Both the hexosans and pentosans were lowest in the foliage (poplar: 13.73 %, birch: 15.35 %) and highest in the stem woods (poplar: 45.86 %, Sappi birch chips: 43.57 %). In straws and grasses, hexosans content were similar (ranging between 32.10 % and 36.68 %) except for the roadside grass (28.83 %). The most interesting observation was that poplar stem wood chips showed the highest hexosan content, which was >5 % and 8 % higher than the beech stem wood and birch stem wood respectively. On the other hand, pentosan content in the poplar stem wood was lower than beech and birch stem wood, which can be considered advantageous for biorefinery applications where cellulose, the primary hexosan, is the key target for a variety of applications. Amongst the straws and grasses tested, the pentosan content was highest in switch grass (24.16 %), followed by wheat straw (21.92 %), corn stover (21.40 %) and rice straw (18.69 %), while, sunflower straw had a lower pentosan content, followed by rapeseed straw and roadside grass. Amongst all the feedstock tested, cocoa pod husks and foliage showed the lowest pentosan content (between 2.86 % and 8.93 %). From these results, sunflower straw, one of the least studied feedstock in terms of biorefinery applications, has the potential, on a compositional basis, to compete with the more studied feedstock such as corn stover, wheat straw and rice stover.

Glucan content in all the feedstock tested was very close to the hexosan content and the xylan content was very close to the pentosan content. This is due to the fact that the hemicellulose fraction of all the feedstock tested is pentose rich and particularly xylan rich which is expected, as they are mostly hardwoods and grass species whose hemicellulose are primarily arabinoxylans (Álvarez et al., 2016). For more details, see Table 3.

However, just xylan and cellulose contents and their ratios are not enough to define the suitability of the feedstock for biorefinery, as there are other factors, such as acetyl content, sugar acids, lignin, and elemental composition, that play significant roles in biomass fractionation and valorisation. Hence, they are studied, correlated and reported in the sections below (Figs. 2 and 3) (Table 2).

Mannose, arabinose, galactose and rhamnose are present in low concentration in most of the samples and hence not presented in detail. Please see Table 4 for the values. Some noteworthy findings from this analysis are 1) high arabinose content in poplar bark (3.49 %) indicating that hemicellulose is made of either arabinoglucuronoxylan or glucuronoarabinoxylan; 2) high galacatose concentration in cocoa pod husk (3.03 %) with no uronic acids (Smith et al., 2017) (Table 4).

Table 2
Total sugars, hexosans and pentosans content of different forestry and agriculture feedstock (included residues and waste).

	Total Sugars (% Dry Mass)				Hexosans (% Dry Mass)				Pentosans (% Dry Mass)			
Sample Name	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*
Beech Bark	41.80	42.06	41.53	*0.38*	19.60	19.69	19.52	*0.12*	14.41	14.51	14.31	*0.14*
Beech Branches	52.72	52.62	52.81	*0.13*	31.90	31.92	31.89	*0.02*	14.71	14.65	14.77	*0.08*
Beech Foliage	34.65	34.56	34.75	*0.13*	19.30	19.30	19.30	*0.00*	8.93	8.94	8.91	*0.02*
Beech Stemwood Chips	63.97	63.98	63.95	*0.02*	39.64	39.73	39.54	*0.13*	19.59	19.51	19.66	*0.11*
Birch Bark	36.49	36.71	36.26	*0.31*	18.32	18.48	18.16	*0.23*	12.70	12.95	12.45	*0.36*
Birch Branches	50.51	50.76	50.25	*0.36*	29.20	29.35	29.04	*0.22*	15.71	15.81	15.62	*0.14*
Birch Foliage	28.89	28.89	28.90	*0.01*	15.35	15.36	15.34	*0.01*	5.46	5.48	5.45	*0.02*
Birch Stemwood Chips	61.95	61.91	61.99	*0.05*	37.02	37.05	37.00	*0.03*	20.22	20.21	20.23	*0.02*
Birch Wood with Bark	55.23	55.26	55.20	*0.04*	33.58	33.58	33.59	*0.00*	17.17	17.15	17.19	*0.03*
Cocoa Pod Husk	26.02	25.97	26.08	*0.08*	23.17	23.12	23.21	*0.06*	2.86	2.84	2.87	*0.02*
Corn Stover Residues	60.15	60.56	59.75	*0.57*	36.68	37.13	36.23	*0.63*	21.40	21.47	21.32	*0.11*
Cow Manure Fibres	44.15	44.09	44.20	*0.08*	24.48	24.40	24.57	*0.12*	17.24	17.17	17.31	*0.10*
Intact Olive Branches	54.80	54.86	54.75	*0.08*	34.53	34.51	34.55	*0.03*	14.49	14.53	14.45	*0.06*
Olive Tree Residues	54.11	54.02	54.19	*0.12*	35.46	35.42	35.50	*0.06*	13.70	13.63	13.77	*0.10*
Poplar Bark	42.29	42.17	42.41	*0.17*	22.31	22.30	22.32	*0.02*	13.19	13.06	13.31	*0.18*
Poplar Branches	49.24	49.45	49.03	*0.29*	30.18	30.25	30.12	*0.10*	13.16	13.18	13.14	*0.03*
Poplar Foliage	26.89	26.59	27.19	*0.42*	13.73	13.54	13.93	*0.28*	7.24	7.15	7.33	*0.13*
Poplar Stemwood Chips	66.18	66.12	66.25	*0.09*	45.86	45.85	45.88	*0.02*	15.93	15.84	16.01	*0.12*
Rapeseed Straw	60.63	60.80	60.46	*0.24*	36.02	36.13	35.91	*0.16*	14.14	14.16	14.11	*0.04*
Rice Straw	53.86	54.07	53.66	*0.30*	33.66	33.76	33.56	*0.15*	18.69	18.74	18.63	*0.08*
Road Side Grass	46.25	46.58	45.91	*0.48*	28.83	28.22	29.45	*0.87*	15.99	15.53	16.46	*0.66*
SAPPI Birch Chips	67.46	67.27	67.65	*0.27*	43.57	43.34	43.79	*0.32*	20.02	19.93	20.10	*0.12*
Sunflower Straw	53.87	53.84	53.89	*0.04*	33.37	33.43	33.31	*0.08*	13.56	13.59	13.54	*0.03*
Switchgrass	56.26	56.18	56.34	*0.11*	32.10	32.05	32.15	*0.07*	24.16	24.13	24.19	*0.04*
Wheat Straw	59.80	59.83	59.77	*0.04*	36.12	36.16	36.08	*0.05*	21.92	21.93	21.91	*0.02*[a]

[a] AV – Average, R1 – Replicate 1, R2 – Replicate 2, SD – Standard Deviation.

Table 3

Uronic acids, glucan and xylan conent of different forestry and agriculture feedstock (included residues and waste).

	Uronic Acids (% Dry Mass)				Glucan (% Dry Mass)				Xylan (% Dry Mass)			
Sample Name	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*
Beech Bark	7.79	7.87	7.70	*0.12*	17.44	17.52	17.37	*0.11*	11.80	11.90	11.69	*0.14*
Beech Branches	6.10	6.05	6.16	*0.07*	29.31	29.34	29.29	*0.04*	13.30	13.25	13.35	*0.07*
Beech Foliage	6.43	6.33	6.53	*0.14*	16.16	16.18	16.15	*0.02*	7.48	7.50	7.46	*0.03*
Beech Stemwood Chips	4.74	4.74	4.75	*0.00*	37.14	37.20	37.07	*0.10*	19.06	18.98	19.14	*0.11*
Birch Bark	5.47	5.27	5.66	*0.27*	16.53	16.74	16.32	*0.30*	10.85	11.13	10.56	*0.41*
Birch Branches	5.60	5.61	5.59	*0.01*	26.22	26.33	26.11	*0.15*	14.45	14.54	14.37	*0.12*
Birch Foliage	8.08	8.05	8.12	*0.05*	10.00	10.05	9.95	*0.07*	3.31	3.32	3.30	*0.01*
Birch Stemwood Chips	4.71	4.66	4.76	*0.07*	34.41	34.41	34.41	*0.00*	19.77	19.76	19.79	*0.02*
Birch Wood with Bark	4.47	4.52	4.42	*0.07*	31.08	31.07	31.09	*0.02*	16.39	16.36	16.41	*0.04*
Cocoa Pod Husk	N.A.	N.D.	N.D.	*N.A.*	15.96	15.90	16.02	*0.08*	1.52	1.52	1.53	*0.01*
Corn Stover Residues	2.07	1.96	2.19	*0.17*	35.29	35.75	34.84	*0.64*	18.46	18.55	18.37	*0.13*
Cow Manure Fibres	2.42	2.51	2.33	*0.13*	23.05	22.98	23.13	*0.11*	15.13	15.07	15.18	*0.08*
Intact Olive Branches	5.79	5.82	5.75	*0.05*	31.44	31.43	31.45	*0.02*	12.39	12.42	12.35	*0.05*
Olive Tree Residues	4.95	4.97	4.92	*0.03*	32.51	32.48	32.54	*0.05*	12.21	12.14	12.28	*0.10*
Poplar Bark	6.79	6.81	6.77	*0.03*	20.29	20.22	20.37	*0.11*	9.69	9.49	9.89	*0.28*
Poplar Branches	5.90	6.01	5.78	*0.16*	28.02	28.06	27.98	*0.06*	11.18	11.21	11.16	*0.03*
Poplar Foliage	5.92	5.91	5.93	*0.01*	11.41	11.28	11.53	*0.18*	4.61	4.55	4.67	*0.09*
Poplar Stemwood	4.40	4.44	4.36	*0.06*	43.65	43.65	43.65	*0.00*	15.40	15.31	15.48	*0.12*
Rapeseed Straw	10.48	10.51	10.44	*0.05*	32.88	32.98	32.77	*0.15*	13.49	13.52	13.45	*0.05*
Rice Straw	1.52	1.57	1.47	*0.07*	32.35	32.42	32.27	*0.11*	16.09	16.14	16.03	*0.07*
Road Side Grass	2.84	2.84	N.D.	*N.A.*	26.87	26.24	27.49	*0.88*	13.35	12.92	13.77	*0.60*
SAPPI Birch	3.88	4.00	3.75	*0.18*	41.37	41.17	41.57	*0.28*	19.72	19.64	19.80	*0.11*
Sunflower Straw	6.94	6.83	7.05	*0.16*	31.02	31.08	30.96	*0.08*	13.22	13.24	13.20	*0.03*
Switchgrass	N.A.	N.D.	N.D.	*N.A.*	31.13	31.10	31.16	*0.04*	21.38	21.35	21.40	*0.04*
Wheat Straw	1.76	1.74	1.77	*0.03*	35.11	35.13	35.09	*0.03*	19.61	19.60	19.62	*0.01*[a]

[a] AV – Average, R1 – Replicate 1, R2 – Replicate 2, SD – Standard Deviation, NA – Not Available, ND – Not Detected.

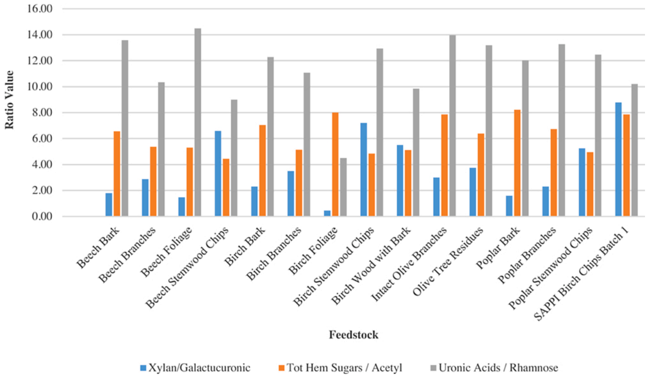

Fig. 2. *Hardwoods Hemicellulose Ratios*. Hemicellulose components ratios (xylan/galacturonic; total hemicellulose sugars/acetyl content; uronic acids/rhamnose) for the hardwoods.

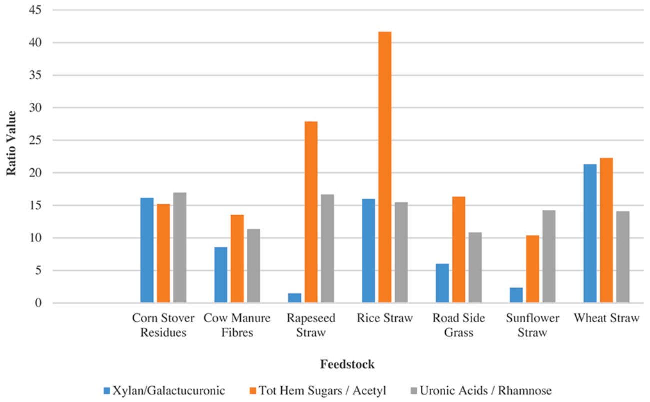

Fig. 3. *Agricultural Residues Hemicellulose Ratios*. Hemicellulose components ratios (xylan/galacturonic; total hemicellulose sugars/acetyl content; uronic acids/rhamnose) for the agricultural residues.

3.3. Uronic acids

The uronic acids concentration varied from limited amounts present in two types of straws (wheat: 1.76 %, rice: 1.52 %) to much higher amount in rapeseed straw (10.48 %). The ratio between xylan to uronic acids is key to note, as the characteristics of xylan in terms of solubility, viscosity and emulsification ability depends on the side chain decorations on the xylan backbone (Olorunsola et al., 2018). Rice straw and corn stover showed highest xylan to uronic acids ratio (10.6 and 8.9 respectively) indicating that they would be more suitable for viscous formulations, while the foliage was highly branched indicating that xylan would be more soluble and less viscous compared with xylan from other sources tested (Ebringerová and Hromádková, 1999).

The most abundant acidic sugar in the feedstock tested was galacturonic acid, which was found to be present in significant quantities in bark and foliage of most feedstock and in some straws (beech bark: 6.61 %, birch foliage: 7.42 %, poplar bark: 6.10 %, rapeseed straw: 9.17 %, sunflower straw: 5.64 %) (Table 5). Glucuronic acid and 4-O-methyl-D-glucuronic acids were present in considerably lower concentrations. Galacturonic acid is generally mostly derived from the pectin fraction in the cell wall, while glucuronic and methyl glucuronic acid are derived from the decorations of the xylan. Acidic sugars not only have industrial applications on their own but also play a significant part, particularly glucuronic acids, in the functionality of xylan extracted for industrial purposes (Lyczakowski et al., 2017).

3.4. Acetyl content

The acetyl groups are the key side chains of xylan and are responsible for some characteristics of xylan such as its solubility (Zhang et al., 2011). In many pre-treatment processes, acetyl side chains are removed from xylan during the process, and recently selective cleavage of acetyl groups from xylan by alkaline treatments to recover acetic acid is under consideration. For this process, alkaline pretreatment is considered most suitable due to the de-esterification ability of alkali reagents (Chen et al., 2012). In addition, acetic acid is the molecule responsible for auto-hydrolysis in the hydrothermal pre-treatments. In such pre-treatments a higher acetyl content is associated with a higher rate of

Table 4
Mannan, arabinan and galacatan content of different forestry and agriculture feedstock (included residues and waste).

	Mannan (% Dry Mass)				Arabinan (% Dry Mass)				Galactan (% Dry Mass)			
Sample Name	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*
Beech Bark	0.40	0.42	0.38	*0.03*	2.61	2.61	2.62	*0.01*	1.19	1.19	1.19	*0.01*
Beech Branches	0.61	0.60	0.62	*0.02*	1.41	1.40	1.42	*0.01*	1.39	1.40	1.38	*0.01*
Beech Foliage	0.80	0.79	0.81	*0.01*	1.45	1.44	1.46	*0.01*	1.89	1.88	1.89	*0.01*
Beech Stemwood Chips	0.90	0.92	0.88	*0.03*	0.53	0.53	0.53	*0.00*	1.08	1.08	1.07	*0.00*
Birch Bark	0.42	0.39	0.45	*0.04*	1.85	1.82	1.89	*0.05*	0.93	0.91	0.94	*0.02*
Birch Branches	1.08	1.10	1.06	*0.03*	1.26	1.27	1.24	*0.02*	1.39	1.40	1.38	*0.02*
Birch Foliage	0.75	0.75	0.75	*0.00*	2.15	2.16	2.15	*0.01*	2.79	2.77	2.82	*0.04*
Birch Stemwood Chips	1.59	1.61	1.57	*0.03*	0.45	0.45	0.44	*0.00*	0.66	0.66	0.67	*0.01*
Birch Wood with Bark	0.87	0.87	0.88	*0.01*	0.78	0.79	0.77	*0.01*	1.18	1.18	1.17	*0.01*
Cocoa Pod Husk	2.28	2.28	2.29	*0.01*	1.33	1.33	1.34	*0.01*	3.03	3.05	3.01	*0.03*
Corn Stover Residues	0.30	0.30	0.30	*0.00*	2.94	2.92	2.96	*0.03*	0.97	0.96	0.98	*0.01*
Cow Manure Fibres	0.48	0.48	0.49	*0.01*	2.11	2.10	2.13	*0.02*	0.73	0.74	0.73	*0.00*
Intact Olive Branches	1.57	1.57	1.57	*0.00*	2.11	2.11	2.10	*0.01*	1.11	1.10	1.12	*0.01*
Olive Tree Residues	1.58	1.57	1.59	*0.02*	1.49	1.49	1.49	*0.00*	0.99	0.98	1.00	*0.01*
Poplar Bark	0.37	0.39	0.34	*0.04*	3.49	3.57	3.42	*0.10*	1.08	1.10	1.07	*0.02*
Poplar Branches	0.66	0.69	0.64	*0.03*	1.98	1.98	1.97	*0.00*	1.06	1.07	1.05	*0.02*
Poplar Foliage	0.47	0.45	0.49	*0.03*	2.63	2.60	2.67	*0.05*	1.36	1.33	1.38	*0.04*
Poplar Stemwood Chips	1.18	1.16	1.19	*0.02*	0.53	0.53	0.53	*0.00*	0.68	0.68	0.68	*0.00*
Rapeseed Straw	1.52	1.53	1.50	*0.02*	0.65	0.64	0.66	*0.01*	0.99	1.00	0.99	*0.01*
Rice Straw	0.22	0.24	0.20	*0.03*	2.60	2.60	2.60	*0.00*	1.00	1.00	0.99	*0.00*
Road Side Grass	0.45	0.47	0.42	*0.03*	2.65	2.60	2.69	*0.06*	1.26	1.26	1.26	*0.00*
SAPPI Birch Chips	1.04	1.02	1.05	*0.02*	0.29	0.29	0.30	*0.01*	0.78	0.77	0.78	*0.01*
Sunflower Straw	1.25	1.24	1.25	*0.00*	0.34	0.34	0.34	*0.00*	0.62	0.62	0.62	*0.00*
Switchgrass	0.08	0.06	0.11	*0.03*	2.78	2.77	2.79	*0.01*	0.77	0.77	0.78	*0.00*
Wheat Straw	0.24	0.24	0.25	*0.01*	2.31	2.34	2.29	*0.03*	0.64	0.65	0.63	*0.02*[a]

[a] AV – Average, R1 – Replicate 1, R2 – Replicate 2, SD – Standard Deviation.

Table 5
Rhamnan, glucoronic acid, 4-O-Methyl-D-Glucuronic Acid and galacturonic acid content of different forestry and agriculture feedstock (included residues and waste).

	Rhamnan (% Dry Mass)				Glucuronic Acid (% Dry Mass)				4-O-Methyl-D-Glucuronic Acid (% Dry Mass)				Galacturonic Acid (% Dry Mass)			
Sample Name	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*
Beech Bark	0.57	0.57	0.58	*0.00*	0.09	0.10	0.09	*0.00*	1.09	1.15	1.02	*0.09*	6.61	6.63	6.59	*0.03*
Beech Branches	0.59	0.58	0.60	*0.01*	0.09	0.09	0.10	*0.01*	1.37	1.36	1.38	*0.01*	4.64	4.61	4.68	*0.05*
Beech Foliage	0.44	0.44	0.45	*0.00*	0.14	0.14	0.15	*0.01*	1.20	1.18	1.22	*0.03*	5.08	5.01	5.15	*0.10*
Beech Stemwood	0.53	0.53	0.52	*0.01*	0.09	0.07	0.11	*0.02*	1.76	1.77	1.75	*0.02*	2.89	2.89	2.89	*0.00*
Birch Bark	0.45	0.44	0.45	*0.01*	0.08	0.08	0.07	*0.00*	0.66	0.56	0.75	*0.13*	4.73	4.63	4.84	*0.15*
Birch Branches	0.51	0.52	0.49	*0.02*	0.12	0.12	0.11	*0.00*	1.34	1.27	1.42	*0.11*	4.14	4.22	4.06	*0.12*
Birch Foliage	1.80	1.79	1.81	*0.02*	0.35	0.36	0.35	*0.01*	0.30	0.25	0.35	*0.07*	7.42	7.44	7.41	*0.02*
Birch Stemwood	0.36	0.37	0.35	*0.01*	0.06	0.05	0.06	*0.01*	1.91	1.86	1.96	*0.07*	2.75	2.75	2.74	*0.01*
Birch Wood + Bark	0.45	0.46	0.45	*0.01*	0.08	0.09	0.06	*0.02*	1.42	1.43	1.41	*0.01*	2.98	3.00	2.95	*0.03*
Cocoa Pod Husk	1.90	1.90	1.90	*0.00*	N.A.	N.D.	N.D.	*N.A.*	N.A.	N.D.	N.D.	*N.A.*	N.A.	N.D.	N.D.	*N.D.*
Corn Stover	0.12	0.12	0.12	*0.00*	0.24	0.23	0.25	*0.01*	0.69	0.62	0.76	*0.10*	1.14	1.11	1.18	*0.05*
Cow Manure	0.21	0.21	0.22	*0.00*	0.19	0.19	0.18	*0.01*	0.47	0.53	0.41	*0.08*	1.77	1.80	1.74	*0.04*
Intact Olive	0.41	0.42	0.41	*0.00*	0.09	0.06	0.11	*0.03*	1.56	1.61	1.52	*0.06*	4.13	4.15	4.12	*0.02*
Olive Tree	0.38	0.38	0.37	*0.01*	0.10	0.10	0.10	*0.01*	1.58	1.57	1.59	*0.01*	3.27	3.29	3.24	*0.04*
Poplar Bark	0.57	0.59	0.54	*0.04*	0.10	0.11	0.09	*0.02*	0.60	0.64	0.56	*0.05*	6.10	6.07	6.13	*0.04*
Poplar Branches	0.44	0.43	0.45	*0.01*	0.08	0.09	0.08	*0.01*	0.95	1.00	0.90	*0.07*	4.87	4.93	4.81	*0.08*
Poplar Foliage	0.50	0.48	0.52	*0.03*	0.23	0.23	0.23	*0.00*	N.A.	N.D.	N.D.	*N.A.*	5.69	5.67	5.70	*0.02*
Poplar Stemwood	0.35	0.35	0.35	*0.00*	0.08	0.07	0.09	*0.01*	1.38	1.37	1.40	*0.02*	2.93	3.00	2.87	*0.09*
Rapeseed Straw	0.63	0.61	0.65	*0.02*	0.28	0.29	0.27	*0.02*	1.03	1.02	1.03	*0.01*	9.17	9.20	9.14	*0.04*
Rice Straw	0.10	0.10	0.09	*0.01*	0.24	0.23	0.25	*0.02*	0.27	0.30	0.25	*0.04*	1.01	1.04	0.97	*0.05*
Road Side Grass	0.26	0.25	0.27	*0.01*	0.23	0.23	N.D.	*N.A.*	0.40	0.40	N.D.	*N.A.*	2.21	2.21	N.D.	*N.A.*
SAPPI Birch Chips	0.38	0.37	0.39	*0.01*	0.09	0.07	0.10	*0.02*	1.54	1.60	1.47	*0.09*	2.25	2.32	2.18	*0.10*
Sunflower Straw	0.49	0.49	0.48	*0.00*	0.55	0.54	0.56	*0.02*	0.74	0.72	0.76	*0.03*	5.64	5.56	5.72	*0.11*
Switchgrass	0.11	0.12	0.11	*0.01*	N.A	N.D.	N.D.	*N.A.*	N.A.	N.D.	N.D.	*N.A.*	N.A.	N.D.	N.D.	*N.A.*
Wheat Straw	0.12	0.13	0.12	*0.01*	0.23	0.22	0.23	*0.01*	0.61	0.59	0.62	*0.02*	0.92	0.92	0.92	*0.00*[a]

[a] AV – Average, R1 – Replicate 1, R2 – Replicate 2, SD – Standard Deviation, NA – Not Available, ND – Not Detected.

Table 6
Acetyl content of different forestry and agriculture feedstock (included residues and waste).

	Acetyl Content (% Dry Mass)			
Sample Name	Average	Replicate #1	Replicate #2	*SD*
Beech Bark	2.53	2.27	2.80	*0.38*
Beech Branches	3.23	3.34	3.11	*0.16*
Beech Foliage	2.28	2.27	2.29	*0.02*
Beech Stemwood Chips	4.97	4.96	4.99	*0.02*
Birch Bark	2.06	1.96	2.15	*0.13*
Birch Branches	3.64	4.00	3.29	*0.51*
Birch Foliage	1.35	1.33	1.36	*0.01*
Birch Stemwood Chips	4.72	4.72	4.72	*0.00*
Birch Wood with Bark	3.85	3.83	3.86	*0.02*
Corn Stover Residues	1.50	2.06	0.93	*0.79*
Cow Manure Fibres	1.38	1.38	1.38	*0.01*
Intact Olive Branches	2.24	2.21	2.27	*0.04*
Olive Tree Residues	2.61	2.57	2.64	*0.05*
Poplar Bark	1.85	1.79	1.91	*0.09*
Poplar Branches	2.28	2.53	2.04	*0.34*
Poplar Foliage	0.86	0.85	0.86	*0.01*
Poplar Stemwood Chips	3.67	3.63	3.72	*0.06*
Rapeseed Straw	0.62	0.63	0.62	*0.00*
Rice Straw	0.48	0.49	0.47	*0.01*
Road Side Grass	1.10	1.06	1.13	*0.05*
SAPPI Birch Chips	2.83	2.89	2.76	*0.09*
Sunflower Straw	1.53	1.53	1.53	*0.00*
Switchgrass	2.56	2.56	2.57	*0.01*
Wheat Straw	1.03	1.00	1.05	*0.03*[a]

[a] SD – Standard Deviation.

auto-hydrolysis, which is considered advantageous since the use of additional catalysts (e.g. acids) can be reduced or avoided (Bassani et al., 2020). Hence, it is key to quantify acetyl content in the feedstock.

Amongst the selected feedstock, the acetyl contents in the herbaceous samples (straws and grasses) were lower (ranging from 0.48 % in rice straw to 1.50 % in corn stover and sunflower straw) than the forestry residues. The foliage, bark and branches had acetyl contents between 2% and 4%, except for poplar foliage, which had a relatively low acetyl content of 0.86 %. The highest acetyl content was found in stem wood chips, ranging between 3.67 % and 4.97 %, with poplar stem wood occupying the lowest point in this range. However, it should be noted that the xylan to acetyl content ratio was lowest in poplar stem wood compared with other stem woods, with the same observed in the case of acidic sugars, indicating that the xylan from poplar stem wood is more decorated than the birch and beech wood. For more details, see Table 6.

3.5. *Lignin content*

Klason lignin was present in considerable amounts in barks and foliage (birch bark: 34.10 %, beech foliage: 29.67 %, poplar foliage: 30.49 %) and in significantly lesser amounts in stem wood chips, straws and grasses (poplar stem wood: 17.00 %, corn stover: 11.06 %, wheat straw: 14.63 %, switchgrass: 14.41 %). The total lignin content in the herbaceous feedstocks was lower (<20 %) with corn stover being the lowest (13 %). Amongst the woody species, olive tree residues and branches had the lowest lignin content (21.3 % and 22.4 % respectively). For more details, see Table 7.

3.6. *Elemental data*

The carbon percentage of dry biomass ranged from 41.32 % (rice straw) to 55.49 % (birch bark), with hydrogen content ranging from 5.07 % (rice straw) to 6.35 % (birch bark), nitrogen content ranging from 0.24 % (poplar and beech stem wood) to 2.95 % (cocoa pod husk), sulphur content ranging from 0.01 % (birch bark and birch stem wood) to 0.92 % (poplar bark), and the oxygen content ranging from 32.11 % (birch foliage) to 43.67 % (Sappi birch chips).

The relevance of this analysis is to understand the properties of biomass at the level of elements, as they give an indication on the application potential of the feedstock. Mostly, the application potential is determined by H:C, O:C, C:N and C:S ratios. All the feedstock tested showed similar H:C ratio, approximately 0.1, which is expected for lignocellulosic biomass (Da Silva et al., 2019). O:C ratios followed the same trends of H:C ratio in all the feedstock. Low H:C and O:C ratio are a good indication for the use of wood as energy (Pereira et al., 2013). On the other hand, C:N ratio and C:S ratio varied significantly. Sulphur content was very low in the biomass tested and hence was not given high

Table 7
Klason lignin, acid-soluble lignin and total lignin content of different forestry and agriculture feedstock (included residues and waste).

	Klason Lignin (% Dry Mass)				Acid Soluble Lignin (% Dry Mass)				Total Lignin (% Dry Mass)			
Sample Name	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*
Beech Bark	30.92	30.94	30.91	*0.02*	1.56	1.56	1.57	*0.00*	32.49	32.50	32.48	*0.01*
Beech Branches	27.73	27.54	27.92	*0.27*	2.25	2.24	2.26	*0.02*	29.98	29.78	30.19	*0.29*
Beech Foliage	29.67	29.54	29.80	*0.18*	2.78	2.77	2.79	*0.01*	32.44	32.30	32.58	*0.20*
Beech Stemwood Chips	21.63	21.71	21.54	*0.12*	2.54	2.50	2.59	*0.06*	24.17	24.21	24.13	*0.06*
Birch Bark	34.10	33.62	34.59	*0.69*	1.20	1.20	1.21	*0.00*	35.31	34.82	35.80	*0.69*
Birch Branches	28.77	29.01	28.54	*0.34*	2.17	2.18	2.17	*0.01*	30.95	31.19	30.70	*0.34*
Birch Foliage	46.22	46.17	46.27	*0.07*	4.41	4.43	4.38	*0.04*	50.62	50.60	50.65	*0.04*
Birch Stemwood Chips	21.91	21.75	22.06	*0.22*	2.58	2.36	2.81	*0.32*	24.49	24.11	24.87	*0.54*
Birch Wood with Bark	23.67	23.65	23.68	*0.02*	2.46	2.50	2.42	*0.05*	26.13	26.15	26.11	*0.03*
Cocoa Pod Husk	24.80	24.67	24.92	*0.18*	3.09	2.93	3.26	*0.23*	27.89	27.60	28.18	*0.41*
Corn Stover Residues	11.06	11.11	11.01	*0.07*	2.14	2.13	2.14	*0.00*	13.19	13.24	13.15	*0.06*
Cow Manure Fibres	25.61	25.30	25.92	*0.43*	1.85	1.87	1.84	*0.02*	27.47	27.17	27.76	*0.41*
Intact Olive Branches	18.86	18.65	19.08	*0.30*	3.57	3.60	3.53	*0.05*	22.43	22.26	22.60	*0.24*
Olive Tree Residues	18.68	18.82	18.54	*0.20*	2.61	2.65	2.57	*0.06*	21.29	21.47	21.11	*0.26*
Poplar Bark	19.86	19.97	19.75	*0.16*	1.79	1.80	1.78	*0.01*	21.65	21.77	21.53	*0.17*
Poplar Branches	23.22	23.33	23.11	*0.15*	1.80	1.78	1.82	*0.02*	25.02	25.11	24.93	*0.13*
Poplar Foliage	30.49	30.39	30.59	*0.15*	2.11	2.08	2.14	*0.04*	32.60	32.46	32.73	*0.19*
Poplar Stemwood Chips	17.00	16.85	17.16	*0.22*	2.44	2.45	2.42	*0.02*	19.44	19.30	19.58	*0.20*
Rapeseed Straw	16.65	16.66	16.64	*0.01*	1.95	1.93	1.97	*0.02*	18.60	18.59	18.61	*0.01*
Rice Straw	11.81	12.04	11.59	*0.32*	1.69	1.68	1.71	*0.02*	13.50	13.71	13.29	*0.30*
Road Side Grass	15.18	15.08	15.28	*0.14*	3.35	3.32	3.37	*0.03*	18.53	18.40	18.65	*0.17*
SAPPI Birch Chips	21.01	20.90	21.11	*0.15*	3.05	3.05	3.05	*0.00*	24.06	23.95	24.17	*0.15*
Sunflower Straw	18.28	18.34	18.22	*0.08*	1.50	1.49	1.51	*0.02*	19.78	19.83	19.74	*0.06*
Switchgrass	14.41	14.49	14.34	*0.10*	2.12	2.09	2.14	*0.04*	16.53	16.57	16.48	*0.06*
Wheat Straw	14.63	14.79	14.47	*0.22*	1.38	1.27	1.49	*0.16*	16.01	16.06	15.96	*0.07*[a]

[a] AV – Average, R1 – Replicate 1, R2 – Replicate 2, SD – Standard Deviation.

Table 8

Elemental composition (dry matter basis) of different forestry and agriculture feedstock (included residues and waste).

	Dry Matter Basis (% Dry Mass)																			
	Carbon				Hydrogen				Nitrogen				Sulphur				Oxygen (by difference)			
Sample Name	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*
Beech Bark	51.83	51.78	51.87	*0.06*	5.99	5.96	6.02	*0.04*	0.57	0.56	0.57	*0.00*	0.03	0.02	0.04	*0.01*	37.35	37.43	37.27	*0.11*
Beech Branch	50.94	50.90	50.98	*0.06*	6.02	5.99	6.06	*0.05*	0.65	0.63	0.68	*0.04*	0.08	0.08	0.07	*0.01*	40.38	40.47	40.28	*0.14*
Beech Foliage	49.32	49.45	49.20	*0.17*	6.18	6.21	6.16	*0.04*	2.73	2.72	2.74	*0.02*	0.14	0.14	0.14	*0.00*	36.42	36.28	36.56	*0.19*
Beech Stem Wood	50.40	50.34	50.46	*0.08*	6.33	6.32	6.34	*0.01*	0.24	0.23	0.25	*0.01*	0.04	0.03	0.04	*0.01*	42.41	42.49	42.33	*0.12*
Birch Bark	55.49	55.67	55.31	*0.25*	6.35	6.47	6.23	*0.17*	0.52	0.52	0.51	*0.01*	0.01	0.01	0.00	*0.01*	35.38	35.07	35.69	*0.44*
Birch Branch	52.68	52.62	52.73	*0.08*	6.19	6.19	6.19	*0.00*	0.59	0.57	0.60	*0.02*	0.02	0.03	0.02	*0.00*	38.87	38.93	38.80	*0.09*
Birch Foliage	54.37	54.55	54.20	*0.25*	6.20	6.21	6.20	*0.00*	2.57	2.57	2.56	*0.00*	0.15	0.14	0.15	*0.00*	32.11	31.94	32.29	*0.25*
Birch Chips	50.28	50.20	50.37	*0.12*	6.08	6.07	6.10	*0.02*	0.25	0.25	0.24	*0.00*	0.01	0.01	0.00	*0.00*	42.98	43.08	42.89	*0.14*
Birch W + B	51.03	51.01	51.04	*0.03*	6.06	6.04	6.07	*0.02*	0.53	0.54	0.52	*0.01*	0.01	0.01	0.00	*0.00*	41.07	41.10	41.05	*0.04*
Cocoa Pod	47.70	47.75	47.64	*0.08*	5.44	5.43	5.44	*0.00*	2.95	2.94	2.95	*0.01*	0.16	0.17	0.16	*0.01*	33.66	33.60	33.71	*0.08*
Corn Stover	45.84	46.00	45.69	*0.21*	5.62	5.65	5.59	*0.04*	0.89	0.90	0.89	*0.00*	0.07	0.07	0.07	*0.00*	40.52	40.34	40.70	*0.26*
Cow Manure	45.84	45.92	45.77	*0.11*	5.38	5.38	5.38	*0.00*	1.96	2.01	1.91	*0.07*	0.43	0.43	0.42	*0.01*	33.88	33.75	34.01	*0.19*
Intact Olive	49.39	49.38	49.40	*0.02*	5.83	5.81	5.85	*0.03*	0.30	0.30	0.29	*0.01*	0.10	0.16	0.04	*0.09*	43.12	43.08	43.16	*0.05*
Olive Tree	49.58	49.69	49.47	*0.16*	5.98	6.00	5.95	*0.03*	0.25	0.26	0.24	*0.01*	0.03	0.04	0.01	*0.02*	42.91	42.75	43.07	*0.23*
Poplar Bark	51.07	51.19	50.94	*0.18*	6.18	6.23	6.13	*0.06*	1.04	1.07	1.01	*0.04*	0.92	1.15	0.68	*0.34*	37.76	37.33	38.20	*0.62*
Poplar Branch	51.59	51.62	51.57	*0.03*	6.20	6.21	6.19	*0.01*	0.69	0.70	0.69	*0.01*	0.04	0.05	0.04	*0.00*	39.22	39.19	39.26	*0.05*
Poplar Foliage	52.73	52.62	52.84	*0.16*	6.18	6.15	6.21	*0.04*	2.47	2.48	2.46	*0.02*	0.16	0.16	0.16	*0.00*	33.25	33.38	33.12	*0.19*
Poplar Stem	49.81	49.65	49.96	*0.22*	6.12	6.16	6.09	*0.05*	0.24	0.24	0.25	*0.01*	0.01	0.01	0.02	*0.01*	43.33	43.46	43.20	*0.18*
Rapeseed Straw	46.45	46.27	46.63	*0.26*	5.73	5.70	5.75	*0.04*	0.88	0.88	0.88	*0.00*	0.42	0.41	0.43	*0.01*	40.30	40.52	40.09	*0.30*
Rice Straw	41.32	41.36	41.28	*0.06*	5.07	5.08	5.07	*0.01*	1.01	1.03	1.00	*0.02*	0.17	0.17	0.16	*0.00*	36.61	36.55	36.67	*0.09*
Road Grass	44.58	44.61	44.55	*0.04*	5.40	5.43	5.38	*0.04*	2.09	2.09	2.09	*0.01*	0.27	0.27	0.27	*0.00*	35.22	35.17	35.27	*0.07*
SAPPI Birch	49.56	49.73	49.38	*0.25*	6.14	6.16	6.13	*0.02*	0.27	0.30	0.25	*0.04*	0.12	0.17	0.08	*0.06*	43.67	43.41	43.93	*0.37*
Sunflower Straw	45.76	45.75	45.76	*0.00*	5.32	5.31	5.34	*0.03*	0.73	0.74	0.73	*0.00*	0.05	0.04	0.05	*0.01*	38.28	38.31	38.26	*0.03*
Switch grass	47.97	48.08	47.86	*0.15*	5.90	5.90	5.90	*0.01*	0.43	0.44	0.43	*0.01*	0.06	0.06	0.05	*0.01*	42.05	41.93	42.17	*0.17*
Wheat Straw	46.13	45.97	46.29	*0.23*	5.61	5.58	5.64	*0.04*	0.72	0.72	0.73	*0.01*	0.08	0.08	0.07	*0.00*	39.91	40.10	39.72	*0.27*[a]

[a] AV – Average, R1 – Replicate 1, R2 – Replicate 2, SD – Standard Deviation.

Table 9
Elemental composition (as received basis) of different forestry and agriculture feedstock (included residues and waste).

	As Received Basis (% Wet Mass)																			
	Carbon				Hydrogen				Nitrogen				Sulphur				Oxygen (by difference)			
Sample Name	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*
Beech Bark	29.47	29.45	29.50	*0.03*	3.41	3.39	3.42	*0.02*	0.32	0.32	0.32	*0.00*	0.02	0.01	0.02	*0.01*	21.24	21.28	21.20	*0.06*
Beech Branches	29.97	29.95	30.00	*0.03*	3.54	3.52	3.57	*0.03*	0.38	0.37	0.40	*0.02*	0.04	0.05	0.04	*0.00*	23.75	23.81	23.70	*0.08*
Beech Foliage	16.87	16.91	16.82	*0.06*	2.11	2.12	2.11	*0.01*	0.93	0.93	0.94	*0.01*	0.05	0.05	0.05	*0.00*	12.45	12.41	12.50	*0.07*
Beech Stem wood	27.03	27.00	27.06	*0.04*	3.40	3.39	3.40	*0.01*	0.13	0.13	0.14	*0.01*	0.02	0.02	0.02	*0.00*	22.74	22.79	22.70	*0.06*
Birch Bark	32.39	32.50	32.29	*0.15*	3.71	3.78	3.64	*0.10*	0.30	0.31	0.30	*0.01*	0.00	0.01	0.00	*0.01*	20.65	20.47	20.83	*0.26*
Birch Branches	30.79	30.76	30.82	*0.04*	3.62	3.62	3.62	*0.00*	0.34	0.34	0.35	*0.01*	0.01	0.02	0.01	*0.00*	22.72	22.76	22.68	*0.05*
Birch Foliage	21.64	21.71	21.57	*0.10*	2.47	2.47	2.47	*0.00*	1.02	1.02	1.02	*0.00*	0.06	0.06	0.06	*0.00*	12.78	12.71	12.85	*0.10*
Birch Chips	27.59	27.54	27.64	*0.07*	3.34	3.33	3.35	*0.01*	0.14	0.14	0.13	*0.00*	0.00	0.00	0.00	*0.00*	23.58	23.64	23.53	*0.07*
Birch W + B	48.60	48.58	48.62	*0.03*	5.77	5.75	5.78	*0.02*	0.51	0.51	0.50	*0.01*	0.01	0.01	0.00	*0.00*	39.12	39.14	39.09	*0.03*
Cocoa Pod Husk	40.95	41.00	40.90	*0.07*	4.67	4.67	4.67	*0.00*	2.53	2.53	2.53	*0.01*	0.14	0.14	0.13	*0.01*	28.90	28.85	28.94	*0.07*
Corn Stover	40.38	40.52	40.25	*0.19*	4.95	4.97	4.93	*0.03*	0.79	0.79	0.79	*0.00*	0.06	0.06	0.06	*0.00*	35.69	35.53	35.85	*0.22*
Cow Manure	44.05	44.12	43.97	*0.10*	5.17	5.17	5.17	*0.00*	1.88	1.93	1.84	*0.07*	0.41	0.41	0.40	*0.01*	32.55	32.43	32.68	*0.18*
Olive Tree	33.83	33.91	33.76	*0.11*	4.08	4.10	4.06	*0.02*	0.17	0.17	0.16	*0.01*	0.02	0.03	0.01	*0.02*	29.29	29.18	29.39	*0.15*
Poplar Bark	25.35	25.41	25.29	*0.09*	3.07	3.09	3.04	*0.03*	0.52	0.53	0.50	*0.02*	0.46	0.57	0.34	*0.17*	18.74	18.53	18.96	*0.31*
Poplar Branches	29.75	29.76	29.74	*0.02*	3.58	3.58	3.57	*0.01*	0.40	0.40	0.40	*0.00*	0.03	0.03	0.02	*0.00*	22.62	22.60	22.64	*0.03*
Poplar Foliage	23.89	23.84	23.94	*0.07*	2.80	2.78	2.81	*0.02*	1.12	1.13	1.12	*0.01*	0.07	0.07	0.07	*0.00*	15.07	15.13	15.01	*0.09*
Poplar Stem	24.59	24.51	24.66	*0.11*	3.02	3.04	3.01	*0.03*	0.12	0.12	0.12	*0.00*	0.01	0.00	0.01	*0.00*	21.39	21.45	21.33	*0.09*
Rapeseed Straw	40.38	40.22	40.53	*0.22*	4.98	4.95	5.00	*0.03*	0.76	0.76	0.76	*0.00*	0.37	0.36	0.37	*0.01*	35.03	35.22	34.84	*0.26*
Rice Straw	37.85	37.89	37.81	*0.05*	4.65	4.65	4.64	*0.01*	0.93	0.94	0.91	*0.02*	0.15	0.15	0.15	*0.00*	33.54	33.48	33.60	*0.08*
Road Grass	39.46	39.48	39.43	*0.04*	4.78	4.81	4.76	*0.04*	1.85	1.85	1.85	*0.01*	0.24	0.24	0.24	*0.00*	31.17	31.13	31.22	*0.06*
SAPPI Birch	35.29	35.42	35.17	*0.18*	4.38	4.38	4.37	*0.01*	0.20	0.21	0.18	*0.03*	0.09	0.12	0.06	*0.04*	31.10	30.92	31.28	*0.26*
Sunflower Straw	40.14	40.14	40.14	*0.00*	4.67	4.65	4.69	*0.02*	0.64	0.65	0.64	*0.00*	0.04	0.04	0.05	*0.01*	33.58	33.60	33.56	*0.03*
Switch grass	44.47	44.57	44.37	*0.14*	5.47	5.47	5.47	*0.01*	0.40	0.40	0.40	*0.01*	0.05	0.06	0.05	*0.01*	38.98	38.87	39.10	*0.16*
Wheat Straw	41.63	41.48	41.77	*0.20*	5.06	5.04	5.09	*0.03*	0.65	0.65	0.66	*0.01*	0.07	0.07	0.07	*0.00*	36.02	36.19	35.84	*0.25*[a]

[a] AV – Average, R1 – Replicate 1, R2 – Replicate 2, SD – Standard Deviation.

Table 10
Elemental composition (dry ash-free basis) of different forestry and agriculture feedstock (included residues and waste).

	Dry Ash-Free Basis (% DAF)																			
	Carbon				Hydrogen				Nitrogen				Sulphur				Oxygen (by difference)			
Sample Name	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*	AV	R1	R2	*SD*
Beech Bark	54.12	54.08	54.16	*0.06*	6.25	6.23	6.28	*0.04*	0.59	0.59	0.59	*0.00*	0.03	0.02	0.04	*0.01*	39.00	39.09	38.92	*0.11*
Beech Branches	51.95	51.90	51.99	*0.06*	6.14	6.11	6.18	*0.05*	0.66	0.64	0.69	*0.04*	0.08	0.08	0.07	*0.01*	41.17	41.27	41.07	*0.14*
Beech Foliage	52.03	52.16	51.90	*0.18*	6.52	6.55	6.49	*0.04*	2.88	2.87	2.89	*0.02*	0.15	0.15	0.15	*0.00*	38.42	38.28	38.56	*0.20*
Beech Stemwood	50.69	50.63	50.75	*0.08*	6.37	6.36	6.38	*0.01*	0.25	0.24	0.26	*0.01*	0.04	0.03	0.04	*0.01*	42.66	42.74	42.57	*0.12*
Birch Bark	56.77	56.96	56.59	*0.26*	6.50	6.62	6.38	*0.17*	0.53	0.54	0.52	*0.01*	0.01	0.01	0.00	*0.01*	36.20	35.88	36.52	*0.45*
Birch Branches	53.57	53.51	53.62	*0.08*	6.29	6.29	6.30	*0.00*	0.60	0.58	0.61	*0.02*	0.03	0.03	0.02	*0.00*	39.52	39.59	39.45	*0.10*
Birch Foliage	56.99	57.18	56.81	*0.26*	6.50	6.50	6.50	*0.00*	2.69	2.69	2.69	*0.00*	0.15	0.15	0.15	*0.00*	33.66	33.48	33.84	*0.26*
Birch Chips	50.48	50.40	50.57	*0.12*	6.11	6.09	6.13	*0.02*	0.25	0.25	0.25	*0.00*	0.01	0.01	0.00	*0.00*	43.15	43.25	43.06	*0.14*
Birch W + B	51.70	51.68	51.72	*0.03*	6.14	6.12	6.15	*0.02*	0.54	0.55	0.53	*0.01*	0.01	0.01	0.00	*0.00*	41.62	41.64	41.59	*0.04*
Cocoa Pod Husk	53.06	53.12	53.00	*0.09*	6.05	6.04	6.05	*0.00*	3.28	3.27	3.28	*0.01*	0.18	0.19	0.17	*0.01*	37.44	37.38	37.50	*0.09*
Corn Stover	49.32	49.49	49.16	*0.23*	6.05	6.07	6.02	*0.04*	0.96	0.96	0.96	*0.00*	0.08	0.08	0.08	*0.00*	43.59	43.40	43.79	*0.27*
Cow Manure	52.39	52.48	52.31	*0.12*	6.15	6.15	6.15	*0.00*	2.24	2.30	2.18	*0.08*	0.49	0.49	0.48	*0.01*	38.73	38.58	38.88	*0.21*
Intact Olive	50.02	50.01	50.03	*0.02*	5.91	5.88	5.93	*0.03*	0.30	0.31	0.29	*0.01*	0.10	0.17	0.04	*0.09*	43.67	43.63	43.71	*0.05*
Olive Tree	50.21	50.32	50.10	*0.16*	6.05	6.08	6.03	*0.03*	0.25	0.26	0.24	*0.01*	0.03	0.04	0.01	*0.02*	43.46	43.30	43.62	*0.23*
Poplar Bark	52.66	52.79	52.53	*0.18*	6.37	6.42	6.33	*0.07*	1.07	1.10	1.04	*0.04*	0.95	1.19	0.70	*0.35*	38.95	38.49	39.40	*0.64*
Poplar Branches	52.78	52.80	52.76	*0.03*	6.34	6.35	6.33	*0.01*	0.71	0.71	0.70	*0.01*	0.04	0.05	0.04	*0.00*	40.13	40.09	40.16	*0.05*
Poplar Foliage	55.63	55.51	55.75	*0.17*	6.52	6.48	6.55	*0.05*	2.61	2.62	2.60	*0.02*	0.17	0.17	0.17	*0.00*	35.08	35.22	34.94	*0.20*
Poplar Stem	50.05	49.89	50.20	*0.22*	6.15	6.19	6.12	*0.05*	0.25	0.24	0.25	*0.01*	0.01	0.01	0.02	*0.01*	43.54	43.67	43.41	*0.18*
Rapeseeed Straw	49.53	49.34	49.73	*0.27*	6.11	6.08	6.14	*0.04*	0.94	0.94	0.94	*0.00*	0.45	0.44	0.46	*0.01*	42.97	43.20	42.75	*0.32*
Rice Straw	49.08	49.13	49.03	*0.07*	6.03	6.03	6.02	*0.01*	1.20	1.22	1.19	*0.02*	0.20	0.20	0.20	*0.00*	43.49	43.42	43.56	*0.10*
Road Grass	50.91	50.95	50.88	*0.05*	6.17	6.20	6.14	*0.05*	2.39	2.38	2.39	*0.01*	0.31	0.31	0.31	*0.00*	40.22	40.16	40.28	*0.08*
SAPPI Birch	49.67	49.85	49.50	*0.25*	6.16	6.17	6.15	*0.02*	0.28	0.30	0.25	*0.04*	0.12	0.17	0.08	*0.06*	43.77	43.51	44.03	*0.37*
Sunflower Straw	50.76	50.76	50.76	*0.00*	5.91	5.89	5.93	*0.03*	0.81	0.82	0.81	*0.00*	0.05	0.05	0.06	*0.01*	42.47	42.50	42.44	*0.04*
Switch grass	49.76	49.87	49.65	*0.16*	6.12	6.12	6.11	*0.01*	0.45	0.45	0.44	*0.01*	0.06	0.06	0.05	*0.01*	43.62	43.49	43.74	*0.18*
Wheat Straw	49.90	49.72	50.07	*0.25*	6.07	6.04	6.10	*0.04*	0.78	0.77	0.79	*0.01*	0.08	0.08	0.08	*0.00*	43.17	43.38	42.96	*0.29*[a]

[a] AV – Average, R1 – Replicate 1, R2 – Replicate 2, SD – Standard Deviation.

importance in the discussion. The C:N ratio was the lowest in foliage, cow manure and road side grass and happened to be very much in the ratio suitable for biogas and agriculture applications (20:1) (Trautmann and Krasny, 2014). The next highest ratios were observed in stovers and straws (between 40.9 and 62.6) but still far above the ranges required for the biogas and agriculture applications (Tables 8–10).

3.7. Extractives data

The extractives content varied widely according to the solvent used to perform the extraction (Fig. 4) and the plant fraction assessed (Figs. 5 and 6). Full extractives (water and ethanol) ranged from 2.66 % (birch chips) to 30.47 % (poplar foliage), while water extractives ranged from 1.77 % (birch chips) to 23.76 % (poplar foliage) and ethanol extractives ranged from 1.65 % (birch chips) to 20.74 % (poplar bark).

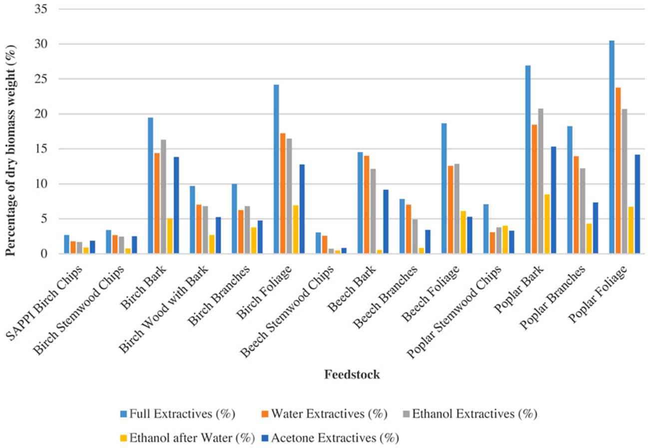

Fig. 4. *Extractives and Solvent Systems.* Extractives in hardwoods fractions according to solvent used for extraction.

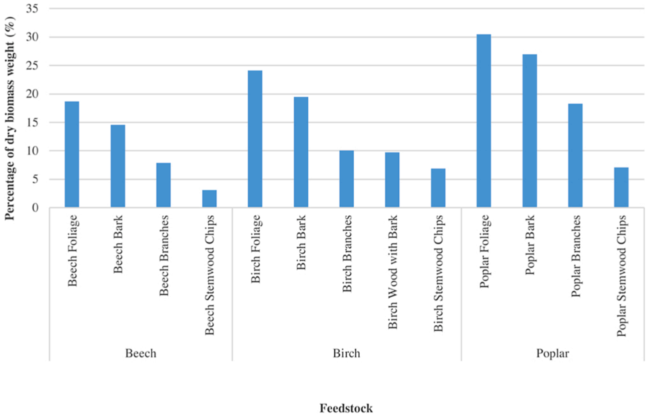

Fig. 5. *Extractives and Species.* Full extractives trends in hardwoods species.

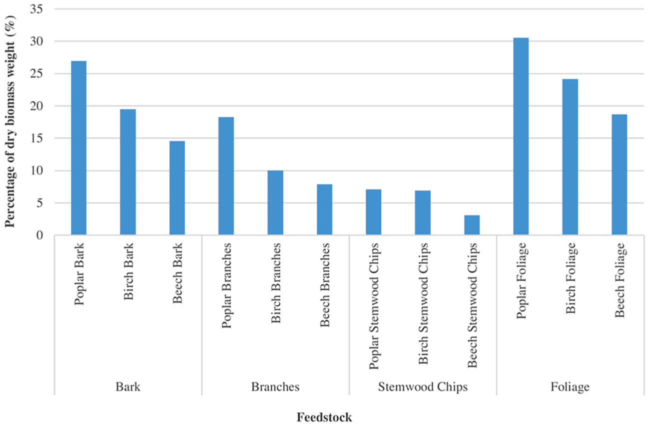

Fig. 6. *Extractives and Fractions.* Full extractives trends in hardwoods fractions.

Ethanol after water extractives (determined as the difference between the full extractives content and the water extractives content) ranged from 0.32 % (intact olive branches) to 6.71 % (poplar foliage) and acetone extractives ranged from 0.82 % (beech stem wood chips) to 15.30 % (poplar bark). For more details, see Table 11.

In the hardwood species, extractives content is highest in foliage and bark fractions and lowest in branches and stem wood. Poplar bark and foliage showed highest extractives content of 30.47 and 26.92 % respectively. Extractives in straws and grasses ranged between 15.30 % and 18.20 %, except for rapeseed straw, which only had 10.56 % extractives (Table 11).

A noteworthy observation is the inverse relationship between the glucan and the extractives contents (Fig. 7). Such relationship is known with lignin and hemicellulose (Garcia-Maraver et al., 2013) but not with extractives. Considering that extractives, if not removed, can cause hindrances in bioconversion process (Li et al., 2015), when using feedstock containing high extractives content, the process should focus on extractives removal and isolation of high value components from extractives.

4. Discussion

4.1. Glucan

In three different hardwoods (birch, beech and poplar) and their fractions, similar trends of glucan were observed. The highest concentration of glucan was obtained in the stem woods, followed by branches, then barks and finally foliage. For the production of cellulose-based products (e.g. glucan-derived biofuels and cellulosic biomolecules), the use of the hardwood stem wood chips is suggested (over 30 % of the feedstock dry weight was determined to be glucan). However, the concentrations of glucan in the branches were still noteworthy and considering that this fraction is currently underutilised, it might be a relevant feedstock for biorefinery processes. In addition, the ratios of glucan content in foliage/branches and barks/woods showed similar trends between the three main hardwood species tested, with ratios foliage/branches of 0.38, 0.55 and 0.40; and ratios bark/wood of 0.48, 0.47 and 0.46 in birch, beech and poplar respectively.

Interesting trends of extractives and glucan content ratios were also observed in the different feedstock and fractions. As seen in Fig. 7, the glucan and the extractives content in the hardwoods fractions proved to be inversely proportional. Higher concentrations of glucan were found in stem wood chips followed by branches, bark and foliage respectively, while higher concentrations of extractives were found in foliage, followed by bark, branches and stem wood chips respectively. These results for the hardwoods proved to be very informative, due to the potential of high extractives contents to interfere with the pre-treatment or enzymatic hydrolysis required for the conversion of glucan into cellulose (Li et al., 2015).

4.2. Hemicellulose

Cellulose obtained from glucan is the strongest polymer in wood, responsible for wood strength due to its elevated level of polymerization and linear orientation. On the other hand, hemicelluloses increase the packing density of the cell wall by acting as a matrix for cellulose. Hemicellulose comprises of sugars and other structural components, such as uronic acids and acetyl side chains. Hemicelluloses and lignin are closely associated, with the primary role of hemicellulose to enable the linkage with the non-crystalline regions of the hydrophilic cellulose and the amorphous areas of the hydrophobic lignin. Furthermore, lignin

Table 11
Extractives contents of selected samples (the data presented are the average of two replicate analyses, with the standard deviation between the two analyses shown in brackets) (N.A.: only one replicate).

		Extractives (% Dry Mass)				
Sample Type	Sample Name	Full Extractives	Water Extractives	Ethanol Extractives	Ethanol after Water	Acetone Extractives
Birch	SAPPI Birch Chips	2.66 (*0.02*)	1.77 (*0.06*)	1.65 (*0.07*)	0.89 (*0.08*)	1.87 (*0.14*)
	Birch Stemwood Chips	3.38 (*0.18*)	2.64 (*0.05*)	2.46 (*0.15*)	0.73 (*0.22*)	2.49 (*0.20*)
	Birch Bark	19.45 (*0.13*)	14.39 (*0.83*)	16.29 (*1.01*)	5.06 (*0.70*)	13.82 (*0.18*)
	Birch Wood with Bark	9.68 (*0.35*)	7.02 (*0.09*)	6.80 (*0.16*)	2.66 (*0.26*)	5.22 (*0.22*)
	Birch Branches	9.99 (*0.03*)	6.24 (*0.38*)	6.80 (*0.03*)	3.75 (*0.41*)	4.75 (*0.18*)
	Birch Foliage	24.16 (*N.A*)	17.23 (*N.A*)	16.46 (*0.23*)	6.90 (*N.A*)	12.75 (*0.40*)
Beech	Beech Stemwood Chips	3.03 (*0.46*)	2.57 (*0.19*)	0.72 (*0.43*)	0.46 (*0.27*)	0.82 (*0.28*)
	Beech Bark	14.52 (*0.69*)	14.00 (*0.01*)	12.11 (*0.02*)	0.52 (*0.68*)	9.15 (*0.09*)
	Beech Branches	7.83 (*0.17*)	7.02 (*0.08*)	4.88 (*0.04*)	0.81 (*0.08*)	3.41 (*0.17*)
	Beech Foliage	18.65 (*0.01*)	12.57 (*0.07*)	12.86 (*1.20*)	6.08 (*0.06*)	5.29 (*0.28*)
Poplar	Poplar Stemwood Chips	7.06 (*0.13*)	3.06 (*0.25*)	3.77 (*0.07*)	4.00 (*0.38*)	3.28 (*0.13*)
	Poplar Bark	26.92 (*0.04*)	18.45 (*0.55*)	20.74 (*0.02*)	8.46 (*0.51*)	15.30 (*0.26*)
	Poplar Branches	18.24 (*0.87*)	13.93 (*0.86*)	12.19 (*0.01*)	4.30 (*0.01*)	7.32 (*0.04*)
	Poplar Foliage	30.47 (*1.09*)	23.76 (*0.14*)	20.70 (*0.17*)	6.71 (*0.95*)	14.17 (*0.03*)
Olive Trees	Olive Tree Residues	17.36 (*0.06*)	14.83 (*0.25*)	11.99 (*0.05*)	2.52 (*0.30*)	6.10 (*0.28*)
	Intact Olive Branches	16.52 (*0.39*)	16.21 (*0.20*)	12.73 (*0.42*)	0.32 (*0.19*)	7.50 (*0.07*)
Grasses	Road Side Grass	17.69 (*0.17*)	17.12 (*0.04*)	7.56 (*0.61*)	0.56 (*0.14*)	2.96 (*0.17*)
	Switchgrass	18.26 (*0.03*)	17.79 (*0.09*)	11.00 (*0.24*)	0.48 (*0.12*)	6.56 (*0.03*)
Straws	Wheat Straw	15.30 (*0.21*)	12.55 (*0.36*)	5.29 (*0.36*)	2.75 (*0.57*)	2.34 (*0.33*)
	Rice Straw	17.69 (*0.62*)	13.63 (*0.07*)	5.38 (*0.59*)	4.06 (*0.55*)	2.20 (*0.23*)
	Sunflower Straw	17.65 (*0.18*)	16.54 (*0.05*)	5.15 (*0.17*)	1.11 (*0.13*)	1.23 (*0.24*)
	Rapeseed Straw	10.56 (*0.29*)	10.12 (*0.25*)	2.88 (*0.07*)	0.43 (*0.04*)	1.78 (*0.05*)
	Corn Stover Residues	16.85 (*0.23*)	15.06 (*0.10*)	6.21 (*0.78*)	1.79 (*0.09*)	3.81 (*0.01*)
Other	Cocoa Pod Husk	22.56 (*N.A*)	19.54 (*N.A*)	10.10 (*0.39*)	3.02 (*N.A*)	5.96 (*0.09*)
	Cow Manure Fibres	12.09 (*0.01*)	7.95 (*0.08*)	3.56 (*0.20*)	4.14 (*0.00*)	2.41 (*0.10*)

holds wood fibres together and helps bind carbohydrates within the cell wall of the wood fibres creating carbohydrates chains (Winandy and Rowell, 1984).

One important role of hemicellulose is the positive effect on biomass digestibility. In Xu et al., 2012, the effects of the three major plant constituents on lignocellulose digestibility were assessed. It was noted that the hydrolysis of hemicelluloses had a positive and directly proportional effect in plant biomass saccharification efficiency, while a negative and inversely proportional effect on lignocellulose crystallinity (Xu et al., 2012).

In the samples analysed, wood hydrolysates predominantly contained glucose and hemicellulose sugars, mainly xylose, while mannose, arabinose, galactose, rhamnose, and sugar acids (e.g., galacturonic and glucuronic acids) were present in lower concentrations. The third most concentrated sugar in the samples was generally arabinose, while mannose and rhamnose contents were significantly lower when compared with the other sugars (Tables 3 and 4). The data indicated that the hemicelluloses present in the samples were mainly made of pentosan sugars (Hayes, 2018), indicating that hemicellulose extracted from the samples tested will be xylan or xylose rich.

The total hemicellulose sugars ranged from 9.57 % (poplar foliage) to 25.13 % (switchgrass) (Fig. 8) and the concentration of uronic acids varied widely amongst the feedstock and their fractions (Fig. 9). Uronic acids are a class of acids, which are made of carbonyl and carboxylic acid functional groups. They are present in plant cell walls and are an output obtained during bioethanol processing (Basumallick and Rohrer, 2017). Polymers containing uronic acids are found in a wide variety of natural occurring polysaccharides, which have been studied for several medical applications. One of the most investigated polymers containing uronic acids is heparin, used for the treatment of thrombosis (Liu and Pedersen, 2007). Also, similarly to hemicellulose, the presence of uronic acids in plant biomass positively affect the enzymatic saccharification and negatively affet the crystallinity of the lignocellulose material. This was demonstrated by the observation of the destruction of cell tissue and the roughness of the residue surface in plant biomass containing high concentration of ammonium oxalate (AO)-extractable uronic acids (Wang et al., 2015).

Interesting trends were noted during the assessment of the xylan to galacturonic acid ratio. In fact, the straws presented the highest xylan to galacturonic ratio; the wood chips the second highest xylan to galacturonic ratio and finally the foliage the lowest (Figs. 2 and 3). Another important ratio that was assessed was the uronic acids content to rhamnose content ratio, which is the most common ratio for the determination of homogalacturonan to rhamnogalacturonan I backbone ratio, and the highest values were encountered in the straws and stovers (Figs. 2 and 3). This ratio is of crucial importance in the determination of potential interactions between pectin, hemicellulose and cellulose structural constituents (Broxterman and Schols, 2018). The results indicate the presence of pectin in grass samples and foliage and necessity of pectinases in lignocellulose enzyme cocktails to achieve complete hydrolysis of biomass.

In cocoa pod husk and switchgrass, uronic acids are not detected, while the maximum concentration of uronic acids was observed in the rapeseed straw sample (10.50 % of the dry biomass weight). Galacturonic acid was determined to be most abundant uronic acid present in the samples. Galacturonic acid is one of the constituents of wood hydrolysates and assessing its concentration is crucial in order to understand the degree of sugar inhibition during fermentation. In fact, according to Huisjes et al. (2012), the yeast *Saccharomyces Cerevisiae*, which is the main producer of bioethanol, cannot use this sugar acid. In addition, it was also noted by Huisjes that galacturonic acid inhibited mostly the fermentation of xylose, while it completely inhibited the fermentation of arabinose (Huisjes et al., 2012). This demonstrates that accurate determination of sugars and the uronic acids in biomass and biomass hydrolysates is important because it allows for the evaluation of the fermentation yields and risk for inhibition during fermentation. (Basumallick and Rohrer, 2017).

Other important hemicellulose structural components are the acetic acid side chains of the sugar groups. Acetyl content is responsible for the changes in solubility of the hemicellulose fraction, with more acetyl content increasing the solubility of the hemicellulose. In fact, the contents of xylose, arabinose and furfural increased as increasing the auto-hydrolysis pretreatment temperature and/or time. Furthermore, as explained by Li et al. (2014), in poplar wood chips, the increased formation of acetic acid decreases the pH of the hydrolysates and has an overriding effect on the dissolution of hemicellulose sugars (Li et al., 2014).

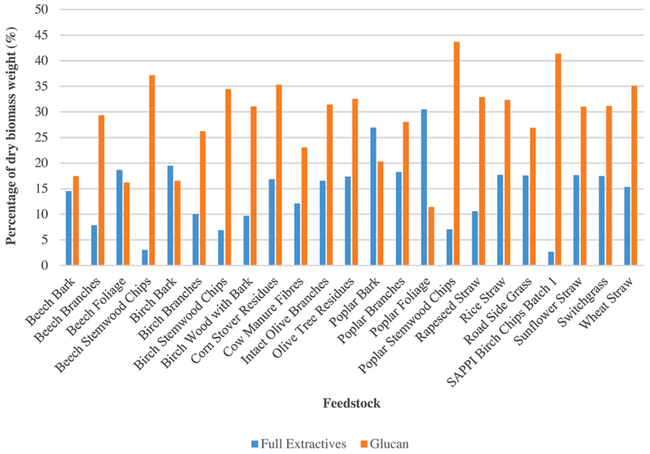

Fig. 7. *Glucan and Extractives*. Glucan and full extractives content in feedstock.

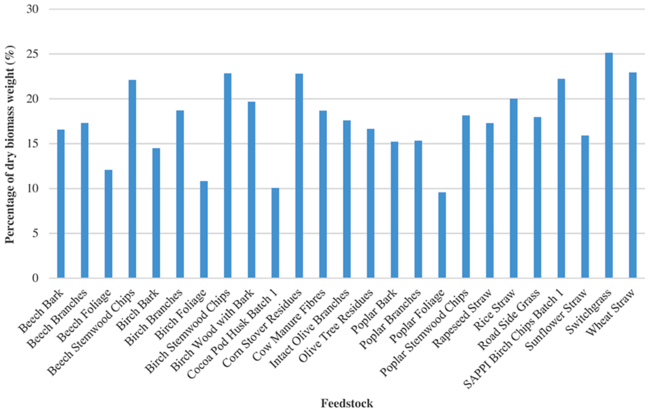

Fig. 8. *Hemicellulose Sugars*. Hemicellulose sugars content in feedstock.

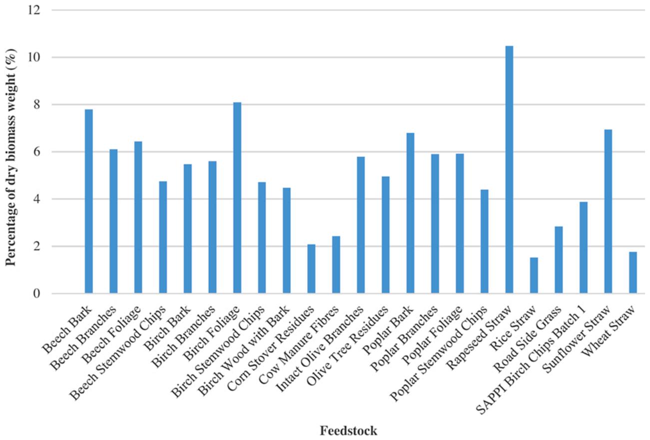

Fig. 9. *Uronic Acids*. Uronic acids content in feedstock.

As showed in the results section, the acetic acid content varied from 0.48 % (rice straw) to 4.72 % (birch stem wood chips). The results are in line with the concentration obtained by Rowell, 2012, in which the acetic acid content of several hardwoods and softwoods was assessed and where it was found that the acetyl content was considerably higher in hardwoods and specifically in stem wood chips, compared with the content determined in other hardwood feedstock (Rowell et al., 2012). On the other hand, the straws, especially rice straw, showed the highest hemicellulose to acetyl content ratio, followed by rapeseed straw and wheat straw (Fig. 6).

Depending on the application, the presence of acetyl groups in the biomass can be advantageous or disadvantageous. For example, acetic acid, which is derived from acetyl groups, is inhibitory for fermentation and hence considered unfavourable for bioconversions, especially for ethanol fermentation (Liu et al., 2017). On the contrary, the presence of acetic acid in wood samples has been proven beneficial to the improvement of certain wood properties during the use phase of wooden products. For example, high concentration of acetic acid have shown to result in a very durable, dimensionally stable and UV-resistant material possessing all the mechanical properties of the untreated wood, but with clear improvements (Beckers et al., 2003).

4.3. *Lignin*

Another important constituent, which affects the properties of the products obtained from biotransformation processes, is lignin. As explained in the results section, the higher concentrations of Klason lignin compared with acid soluble lignin gave indication of the presence of more recoverable lignin in the feedstock assessed.

Lignin is a sustainable alternative source for biofuel production, but it also shows great potential for a wide variety of applications. For example, lignin derivatives such as lignosulfonates are currently used to improve the charge acceptance, high temperature and durability performance of lead-acid batteries, as well as being used as a non-toxic dust control agent, compared with the more commonly used chloride salts and petroleum-based materials (Kienberger, 2019). Furthermore, lignin is utilised in a wide variety of applications, such as the production of lignin-based additives in concrete and resins. More recently, studies have also assessed the suitability of lignin as a renewable macromolecular building block for the development of drug encapsulation and scaffold materials (Witzler et al., 2018).

4.4. *Extractives and thermal properties*

During the extraction process, some difficulties were encountered with the birch foliage and the cocoa pod husks samples. The samples caused the extraction cells to be blocked repeatedly preventing the completion of the full extraction. The lignocellulosic data presented in the results for the birch foliage and cocoa pod husks were therefore based on the hydrolysis of the non-extracted sample and on the ethanol-extracted sample for the cocoa pod husks (Hayes, 2018). The reason for the blockage was possibly due to the presence of either pectin or lipids in high concentration in the cocoa pod husk samples, which caused the formation of a strong layer at the bottom of the extraction cell, which prevented the purging of solvent (Jansen et al., 2006).

According to Pettersen (1984), hardwoods possess generally an elemental composition of approximately 50 % carbon, 6 % hydrogen, 44 % oxygen, and trace amounts of several metal ions (Pettersen, 1984). The elemental composition obtained for the feedstock analysed in this research showed similar results with the carbon ranging from 41.32 % (rice straw) to 55.49 % (birch bark), the hydrogen from 5.07 % (rice straw) to 6.35 % (birch bark) and the oxygen from 32.11 % (birch foliage) to 43.67 % (Sappi birch chips).

Furthermore, in order to use hardwoods as an environmental sensor, the average elemental composition needs to be assessed, taking into consideration that it depends on the species. Esch, 1996, determined the elemental composition of more than 10 samples from almost as many sites for beech and oak and correlated the influence of the growing site with the elemental concentrations. The research concluded that the elemental analysis of wood from trees could be used as an indicator for the presence of soil pollution (Esch et al., 1996). Other studies, like the one performed by Inari, 2009, have focused on the correlation between heat treatments and elemental composition. For example, it was noted that the oxygen content decreased with treatment intensity and was directly proportional to treatment time. At the same time, carbon content increase indicated the formation of carbonaceous materials within the hardwood (Inari et al., 2009).

It is also important to consider how other parameters such as moisture, ash and extractives contents directly affect the thermal properties of the biomass. For example, moisture generally decreases the as-received heating value of the sample due to the effect of water, however the higher the extractives content, the higher the heating value. High ash content of a plant makes it less desirable for conversion into fuel, while high organic extractives content improves the desirability of the sample for fuel production processes (Demirbas, 2002). In the samples analysed the hardwood foliage presented the best characteristics for the production of fuels, having very high extractives content accompanied by relative low ash content (e.g. poplar foliage: extractives content 30.47 %, ash content 2.36 %). In addition, birch, beech and olive showed similar characteristics. Straws and stovers showed lower extractives contents and higher ash contents (e.g. wheat straw: extractives content 15.30 %, ash content 6.81 %) but were still deemed valuable for biofuel production processes. Processed cow manure and rice straw showed the same amounts of extractives and ash respectively (approximately 10 %), therefore were not considered suitable for fuel production (Fig. 1).

4.5. *Trends in hardwood plant fractions*

The analysis also assessed the compositional difference between different fractions (stem wood chips, bark, branches and foliage) for the three main hardwood feedstock (birch, beech, poplar) (Figs. 5 and 6). Several compositional trends were observed and determined to be consistent between the three feedstock. For example, bark and foliage showed higher extractive concentrations but lower sugars content than the stem wood samples (Fig. 10). On the other hand, branches showed a tendency to have lower amounts of sugars but more Klason lignin than the stem wood samples. Also, a considerable content of total hexosans was found in several of the woody biomass species used in this research, with poplar stemwood chips having the highest concentration (45.86 %). High hemicellulose concentration have been demonstrated to positively affect the enzymatic saccharification of biomass, which adds to their desirability for biobased applications. Considering all the forestry residues analysed in this research, the results obtained for poplar were the most promising in terms of enzymatic saccharification, which is in line with the results obtained by Lv et al. (2020), where the species of poplar *Populus simonii* showed the highest hexoses yields using several pretreatments compared with six other woody plants (two other *Populus*, two *Salix* and two *Eucalyptus*). One of the pre-treatment (mild and green) produced more than 70 % cellulose degradation into fermentable hexosans in the *Populus simonii* species and only approximately 30 % cellulose degradation in the other six plants (Lv et al., 2020). The ash contents showed interesting trends amongst the three different species, with lower concentrations in the debarked stem wood chips, slightly higher in the non-debarked stem wood chips, followed by again slightly higher levels in the branches and bark and even higher in the foliage. The samples containing high ash contents typically showed higher extractives contents as well (Hayes, 2018; Moulin, 2017).

4.6. *Trends in herbaceous feedstock*

The analysis focused also on the compositional differences between straws, stover and grasses analysed, with major focus on underutilised feedstock such as sunflower straw and rapeseed straw. As clear from Fig. 11, sunflower and rapeseed straw show very similar lignocellulosic composition characteristics to other feedstock, such as wheat straw and corn stover, which are more commonly used for the production of ethanol and biogas (Passoth and Sandgren, 2019). The results indicate that sunflower straw and rapeseed straw could be used instead of, or alongside, the more common herbaceous feedstock (i.e. wheat straws and corn stover) for the above-mentioned applications.

It was also noted that both roadside grass and switchgrass presented similar characteristics to the straws analysed in this research in terms of the main lignocellulosic constituents (hemicellulose, cellulose, lignin and extractives). According to Glithero et al., 2013, the energy efficiency of biofuels produced from grasses is usually lower than biofuel produced from straws. The biofuel energy efficiency depends on the total sugar content of the feedstock used. In fact, the total sugars content in switchgrass was determined to be quite similar to the straws; however, the roadside grass presented a substantially lower total sugar content (Glithero et al., 2013). However, the presence in grasses of the main lignocellulosic constituents in similar concentration to the straws, gives indication that grasses could be a good substitute of straws for the production of biofuels.

Finally, in Wang et al. (2016), the composition of several bioenergy plants was thoroughly investigated, and few of those plants were also analysed in this research. For example switchgrass, rice, wheat and maize straw were assessed by Wang exhaustively using literature data for cellulose, hemicellulose and lignin content. The results show similar trends to the concentrations found in this research, with wheat straw and corn stover having the highest cellulose contents and switchgrass having the highest hemicellulose concentrations (Wang et al., 2016). However, even if similar trends were noted, the concentrations discussed in this paper were found to be higher for each of the constituents investigated by Wang, giving a positive indication on the efficiency of the methodology used for the analysis.

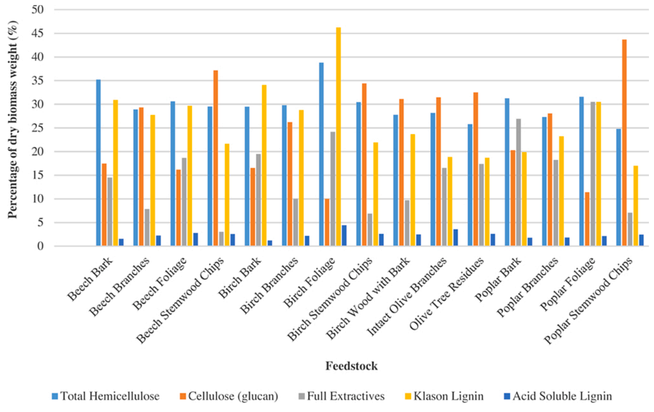

Fig. 10. *Major Constituents Concentrations in Hardwoods.* Concentration trends of major lignocellulosic constituents (hemicellulose, cellulose, extractives, and lignin) in hardwoods.

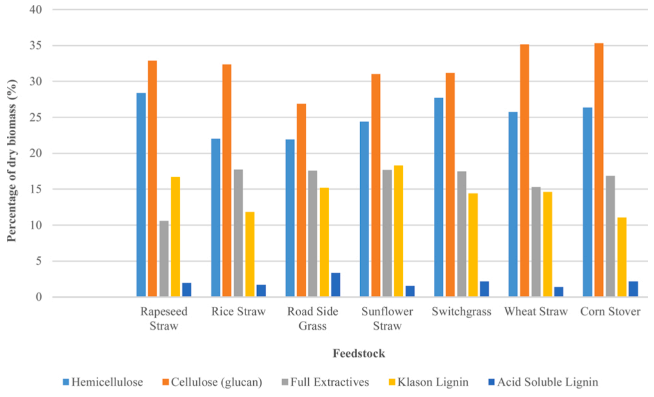

Fig. 11. *Major Constituents Concentrations in Agricultural Residues.* Concentration trends of major lignocellulosic constituents (hemicellulose, cellulose, extractives, and lignin) in agricultural residues.

5. Conclusion

There is an incredible array of potential biomass feedstock to be used for conversion to biofuels and for the production of biochemicals and biopolymers. The feedstock, as can be seen from the results, differ substantially in their composition. Those differences affect greatly the conversion technologies to be applied in order to transform the biomass sources into final products.

Biomass is usually classified under either organic waste or residue from forestry or agriculture, or as an energy crop. Focusing on the forestry and agricultural residues selected for the research, the stem wood of Northern European forestry plants, such as beech, birch and poplar and straws, stover and grasses showed a higher concentration of sugars compared with the hardwoods' barks and foliage. The results also indicated that there is a high variation in the type of hemicelluloses and their correlation with other constituents, such as lignin and extractives, which will dictate the type of technologies to be used for the targeted products.

It is definitely crucial to assess not only the type of feedstock to be used for a specific conversion process, but also which part of the feedstock has the most suitable characteristics and composition for the type of conversion that is performed and the required output. For example, feedstock with high total sugars content, such as the stemwood chips, especially poplar, are suitable for biofuel production due to their demonstrated energy efficiency and ability to positively affect enzymatic saccharification. However, they also contain elevate acetyl contents, and therefore care needs to be taken for certain transformation activities, such as the production of bioethanol, due to the inhibition property of acetic acid during fermentation processes (high concentration of galacturonic acid can also contribute to the inhibition of xylose and arabinose fermentation). Furthermore, other fractions such as foliage presented promising characteristics for fuel production, with high extractives contents, but relatively low ash and acetyl contents, which commonly cause issues in fuel transformation activities. On another note, feedstock containing high lignin contents such as barks and foliage could be used in the production of building and pharmaceutical materials, while it has been demonstrated that sunflower, rapeseed and rice straw present similar compositional characteristics, which make them as suitable as the much more used wheat straw for the production of biofuels and biogas.

In conclusion, the results obtained will be used to build a foundation for a more comprehensive database of wood properties, which will help develop strategies for the selection of feedstock to be used in biorefinery settings.

CRediT authorship contribution statement

Italo Pisanó: Conceptualization, Investigation, Formal analysis, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Lalitha Gottumukkala:** Writing - review & editing, Supervision. **Daniel J. Hayes:** Writing - review & editing, Methodology, Supervision. **James J. Leahy:** Methodology, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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