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Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass

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Abstract

Biomass energy uses organic matter such as wood or plants - lignocellulosic biomass - for creating heat, generating electricity and producing green oil for cars. Modern biomass energy recycles organic leftovers from forestry and agriculture, like corn stovers, rice husks, wood waste and pressed sugar cane, or uses special, fast-growing “energy crops” like willow and switchgrass, as fuel. Biomass is composed of three major components: cellulose, hemicelluloses, and lignin. Their differences in chemical structures lead to different chemical reactivities, making the relative composition in cellulose, hemicelluloses and lignin in the biomass a crucial factor for process design. In this paper thermogravimetric analysis is investigated as a new method to obtain lignin, hemicellulose and α -cellulose contents in biomass. It is shown that this alternative method lead to comparable results than common methods used for the determination of the α -cellulose content, with an enhancement of the accuracy in the determination of the hemicellulose content. Unfortunately, this method cannot be adopted for the determination of the lignin amount.

Keywords : Biomass / Thermogravimetric analysis (TGA) / Cellulose / Lignocellulosic composition / Chemical wet extraction / Klason lignin

1. Introduction

The major chemical components of lignocellulosic biomass are cellulose, hemicelluloses and lignin. Cellulose is a linear polymer of anhydroglucopyranose units linked by ether bonds. Hemicelluloses, as cellulose, are polymers constituted of sugar units. They differ from cellulose by being smaller and branched polymers usually containing more than one sugar type; they are also amorphous polysaccharides. Lignin is a complex, crosslinked, three-dimensional polymer formed with phenylpropane units [1,2]. The chemical differences

between these components directly influence their chemical reactivities. This is why the knowledge of the total amount of each component is crucial to foresee the efficiency of a biomass conversion process [1,3–5]. Knowing accurately the chemical composition of complex lignocellulosic biomass is getting increasing importance for enabling process commercialization converting biomass into green fuels or valuable chemicals.

For this purpose, numerous wet chemical analytical methods are based on the fractionation of biomass samples with further isolation of purified fractions that can be

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quantified using conventional analytical instruments. These analytical procedures are standardized by the American Society for Testing and Materials (ASTM) and the Technical Association of the Pulp and Paper Industry (TAPPI). Despite their accuracy and robustness, these methods cannot be applied in a commercial setting, for they are expensive and time consuming. The recent development of analytical methods using software to extract chemical information from spectroscopic data allows reducing time and cost. For instance, the use of Near Infrared Reflectance (NIR) spectroscopy leads to successful results for the analysis of the composition and of the nutritive value of plant materials such as crude fat, protein, carbohydrate and crude fibres [6–13]. The high reproducibility of NIR analysis is a real advantage. Indeed, testing has demonstrated that NIR spectrometer reproducibility limits contributed for less than 0.1% to the absolute prediction errors through this rapid analysis method. Unfortunately, NIR technique requires large high quality data collection and an initial blank spectrum, limiting to date its use for such applications.

Numerous works deal with the use of thermogravimetric analysis (TGA) of plant biomass for determining thermal decomposition mechanisms. The purpose stands in evaluating the rate of pyrolysis for preventing the risk of forest fire [14,15]. TGA can be coupled to a spectrometer for improving the understanding of the thermal decomposition mechanisms and to estimate the amounts of biogas - such as methane and hydrogen - produced during the pyrolytic process [16,17]. TGA can quantitatively resolve complex mixtures because of the characteristic thermal decomposition temperature of each component [18]. It is well established for instance that the pyrolytic decomposition of woody plant tissues in inert atmospheres occurs at mild temperatures for hemicelluloses (250–300 °C) followed by cellulose (300–350 °C) and finally lignin (300–500 °C) [19]. Moreover, the combination of TGA and differential thermogravimetric analyses (DTG) allows obtaining the lignin content [20] and particularly its influence during the combustion process. Finally, cellulose and lignin contents of pulp and paper have been determined by TGA especially in the description of the biomass pyrolysis leading unfortunately to high errors on hemicelluloses contents [21]. In view of these studies, TGA turns out to be a powerful tool for these analytical purposes.

This study aims at providing an alternative method for biomass analysis that is faster, easier to use and less expensive than existing techniques and methods with comparable or enhanced accuracy.

The present work was led according to the following steps:

- Characterization and chemical analysis of biomass samples: elementary composition and lignocellulosic compositions obtained with wet chemical methods;
- Thermal analysis performed in an inert atmosphere: the TGA and DTG curves of the samples were compared;
- Evaluation of all the experimental data, particularly by identifying the main meaningful correlations between lignin, α -cellulose and hemicelluloses amounts obtained by common methods (wet chemical methods) and by thermogravimetric analysis.

2. Material and methods

2.1. Material

The development of the new method based on TGA for fast and easy determination of real biomass composition was carried out on two different materials: one poplar wood (*Populus nigra* L.) and one fern (*Pteris vittata* L.), both being milled before analyses. These plants were developed for the decontamination of sites under phytoextraction [22].

Industrial high quality cellulose pulps (5092, 5094, 5096, 110106) supplied by Tembec Tartas (France) are produced by acid sulfite pulping process from the softwood “pin maritime” and exhibit a known α -cellulose content (precision of 0.3–0.5%).

The cotton sample called “Cotton Linter Pulp” (Oxley Trading Limited N°20080101) was received from Bergerac NC. Its characteristics are the following ones: dry matter 93.4%, R18 = 99%, and R10 97.5%.

2.2. Characterization

The main characteristic of the initial biomass samples, i.e. elementary composition and particle size were investigated with a CHNS-O Analyzer model 2400 from Perkin Elmer and a laser Malvern 2000S, respectively.

The amount of moisture was determined using the following procedure: 5 g of each sample were added to vials, which were weighted beforehand. The vials were placed in an oven at 105 °C and dried before being transferred into a desiccator for 1 h and re-weighted to determine the percentage of moisture.

The thermogravimetric analyses were carried out in a TAG 2400 Setaram thermobalance, which was coupled to a thermobar Balzers quadrupole mass spectrometer. The ion source was operated at 70 eV. To prevent heat and mass transfer limitations, small samples (5 and 10 mg) were used. The experiments were performed under argon flow (2 L h⁻¹) using a slow temperature increase (5 °C min⁻¹). Samples were heated from room temperature to 700 °C, where they remained for 30 min. Weight loss and heating rate were continuously recorded along the experiment.

The Scanning Electron Microscopy (SEM) equipment used was a JEOL 840 A. Samples were previously coated with a very thin layer of Au/Pd. The SEM has a magnification range from 50 to 50000 and a resolution of 100 nm.

2.3. Fractionation of biomass

Historically, the determination of biomass compositions was mainly carried out in two industrial sectors: the wood and the food industry. Both have developed their own experimental procedures to quantify the amount of α -cellulose, hemicelluloses and lignin. In this paragraph, the first wet chemical methods described are those used in the wood industry sector (part 2.3.1 to 2.3.5). The following ones are those used in the food processing industry (part 2.3.6 to 2.3.9). All these experiments have been subcontracted to a private laboratory. Our wet chemical analyses have been carried out in the laboratory

“Unité Sciences du Bois et des Biopolymères” according to the wood industry sector methods.

2.3.1. Pre-treatment 1

A 16 h Soxhlet extraction with acetone is employed to remove compounds, which are not part of the wood substance or biomass and which may interfere with some analyses. These substances named extractives are waxes, fats, resins, gums, sugars, starches, pitch, sterols, flavonoids, tannins, terpenes, quinones, non-structural sugars, chlorophyll and many other minor building block reserves that vary seasonably and according to the biomass type.

2.3.2. Lignin extraction (LIG)

The lignin content of biomass samples is determined in accordance with Tappi T222 om-88 [23]. In this method, lignin known as “Klason lignin” is defined as the wood component insoluble in a 72% sulphuric acid solution. 1 g of extractive-free biomass is treated with 72% H₂SO₄ solution (15 cm³) for 2 h at room temperature to hydrolyze and solubilize the carbohydrates. The sample is then diluted with water (560 cm³) to reduce the sulphuric acid concentration to 3 wt% and further boiled for 4 h. Next, lignin is allowed to settle before being filtered. The residue is washed using hot water until reaching a neutral pH. The dried insoluble residue represents the lignin content. The sulphuric acid method is the most widely accepted analytical method for determining the lignin content in woody plants, although it is time consuming.

2.3.3. Holocellulose extraction (HOLO)

Ideally, holocellulose contains only cellulose and hemicelluloses. From an experimental point of view during the preparation of holocellulose, the loss of some carbohydrates and a possible retention of the lignin may occur. The procedure used for preparing holocellulose involves the treatment of the milled extractive free wood (4 g) with an acid solution (160 cm³ sodium acetate solution) at 75 °C for 5 h. Sodium chlorite (4 cm³) is added every hour during 4 h. The mixture is then cooled down and the residue is filtered and washed with water first (1 dm³) and with acetone (15 cm³). The residue is finally dried at room temperature; an aliquot is weighted and dried at 105 °C for the determination of the holocellulose content. The first step subjects the biomass sample to a concentrated acid that disrupts the non-covalent interactions between biomass polymers. The second step permits the

optimization of the whole polymer hydrolysis while minimizing the degradation of monomeric sugars. It must be pointed out that degradations of sugars are unavoidable during these two steps of hydrolysis.

2.3.4. α -Cellulose extraction (α)

α -cellulose is defined as the residue of holocellulose insoluble in a 17.5 wt% NaOH solution. It is considered to represent the undamaged higher molecular weight cellulose in the wood or biomass sample. 5 g of holocellulose are added to a 17.5 wt% NaOH solution (100 cm³) at room temperature for a 30 min incubating period. The residue was filtered and washed firstly with water (two times with 200 cm³) and then filtered again. Then, the addition of 15 cm³ of a 10 wt% acetic acid solution served at hydrolyzing the degraded cellulose and hemicelluloses. The residue was filtered and washed with hot water (500 cm³), and dried at 105 °C. The amount of α -cellulose was finally determined gravimetrically. Hemicelluloses are more readily hydrolyzed compared to cellulose because of its branched and amorphous nature.

2.3.5. α -Cellulose extraction (method used for cellulose pulps) (R18)

For bleached and delignified pulp, the level of cellulose purity is obtained by R10, R18, S10 and S18 methods. The values represent the pulp’s solubility in 10% and 18% NaOH solutions under specified conditions (standard ISO 692:1982). The soluble portion (%) of pulp in 10% and 18% NaOH is referred to as S10 and S18, respectively, while the residual fraction (%) is referred to as R10 and R18. It is known that a 10% NaOH solution can dissolve the degraded cellulose and hemicelluloses (S10), whereas a 18% NaOH solution dissolves the most important part of hemicelluloses (S18). The subtraction, S10-S18 (or R18-R10), is a measure of the degraded cellulose, S18 (or 100-R18) represents hemicelluloses and R10 corresponds to α -cellulose and represents the “long-chain” cellulose content.

In the food industry, laboratories generally use the sequential procedure of Van Soest to get the lignocellulosic composition of the forage for animal food [24]. The pre-treatment 1 (see 2.3.1) is not used in the food industry.

2.3.6. Neutral detergent fibre (NDF and NDFB)

NDF and NDFB are the organic matter not solubilized after 1 h under reflux in a neutral detergent solution consisting of sodium laurylsulphate in presence of a 98 °C thermoresistant

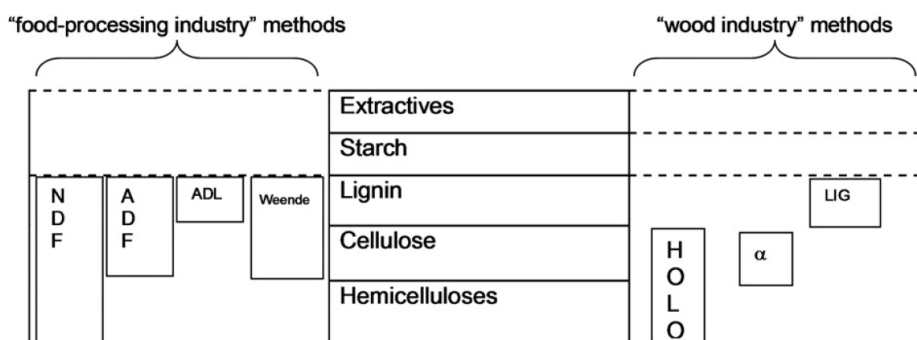


Fig. 1 – Synthetic sketch of each extraction technique allowing accessing the biomass composition.

Table 1 – Elementary analysis of biomass.

Biomass	Particle size	Dry matter (wt% dry)	C H N S				O (from difference) (wt% dry)
			(wt% dry)				
Poplar <i>Populus nigra</i> L.	380–420 μm	96.4 \pm 0.6	48.2 \pm 1.0	6.1 \pm 0.2	0.90 \pm 0.09	0.41 \pm 0.20	42 \pm 2
Fern <i>Pteris Vittata</i> L.	294–310 μm	90.6 \pm 0.5	49.0 \pm 0.1	5.7 \pm 0.2	1.5 \pm 0.3	1.4 \pm 0.1	40 \pm 1
Cellulose pulps	Fibers		41.0	6.1	–	–	52

amylase (Pre-treatment 2). The residue is directly filtered, washed with hot water and dried with acetone. A 550 °C calcination step allowed determining the ash content. NDF includes hemicelluloses, cellulose, lignin, and ash, while NDFB includes only hemicelluloses, cellulose and lignin.

2.3.7. Acid detergent fibre (ADF and ADFB)

ADF and ADFB are the organic matter not solubilized after 1 h under reflux in an acid detergent solution consisting of acetyltrimethylammonium bromide in 0.5 M sulphuric acid. The residue was filtered and washed with hot water and dried with acetone. A new step of calcination allowed determining the ash content. ADF includes cellulose, lignin, and ash. ADFB includes only cellulose and lignin.

2.3.8. Acid detergent lignin (ADL and ADLB)

ADL and ADLB are the organic matter not solubilized after 3 h of extraction with a 72 wt% sulphuric acid solution, i.e. the amount of lignin. Therefore, the hemicelluloses content could be obtained by subtracting the value of ADF from the value of NDF. The amount of cellulose is obtained by the difference between the values of ADF and ADL [25]. Finally, ADLB corresponds to the lignin fraction without ash.

2.3.9. Weende method [26]

The Weende method is quick, simple, inexpensive, and frequently used all over the world in the food industry sector. This technique extracts a fibre residue, “the crude fibre”, after an acidic hydrolysis with a 1.25% H_2SO_4 solution for 30 min under reflux, followed by a basic hydrolysis with a 1.25% NaOH solution for 30 min under reflux. The residue is filtered and washed with hot water. It is then calcinated at 550 °C after being dried at 105 °C. The residue corresponds partly to a mixture of cellulose, lignin, cutin, and suberin.

The Fig. 1 summarizes the various techniques presented in this paragraph.

3. Results and discussions

3.1. Initial characterization

3.1.1. C,H,N,S-O determination

Table 1 gives the elementary analysis of the fern, the poplar, and cellulose pulps. Crude biomasses, fern and wood, have an elementary composition close to the classical value for lignocellulosic biomass. Note the absence of nitrogen and sulphur for the cellulose pulps, which could be attributed to small values out of the detection limit, as previously reported by Kumar et al. for the corn stovers [27]. The granulometric analysis shows a somewhat homogeneous particle size distribution around 300 μm . Milling crude biomass leads to reproducible samples for analysis.

3.1.2. Lignocellulosic composition

The results of the lignocellulosic compositions are presented in Tables 2 and 3 for poplar wood and fern, respectively. The analyses have been performed with the different methods described previously (see Section 2).

The main differences obtained for the fern and wood values in Tables 2 and 3 can be explained by the use of different fractionation methods described in Section 2.

3.1.2.1. Pretreatment. The main difference between the two pre-treatment steps (pre-treatments 1 and 2) was the use of a detergent in the latter. This pre-extraction step, carried out with amylolytic enzymes, actually modifies the chemical properties of the lignocellulosic materials, as it weakens its structure [30].

3.1.2.2. Lignin determination (LIG, ADL and ADLB). Concerning wood biomass, although the lignin content obtained in this work (25 wt%) is close to those found for other wood

Table 2 – Yield of lignin, holocellulose, hemicelluloses and cellulose from poplar wood. Extraction methods used: (a) (LIG), (b) (ADLB), (c) (HOLO), (d) (HOLO- α), (e) (α), (f) (NDFB–ADFB), (g) (ADFB–ADLB) and (h) unknown. (INPT) Institut national polytechnique de Toulouse.

Method	Lignin (wt% dry)	Holocellulose (wt% dry)	Calculated hemicelluloses (wt% dry)	α -cellulose (wt% dry)	Extractibles (wt% dry)	Dry matter (%)
This work: “wood-industry” method	25 \pm 2 (a)	71 \pm 5 (c)	28 \pm 10 (d)	43 \pm 5 (e)	5 \pm 3	96 \pm 3
“Food-industry” method	16 \pm 4 (b)		9 \pm 4 (f)	41 \pm 16 (g)		97
INPT [22]	23 (h)		21 (h)	51 (h)		
Softwoods [28]	35–25 (h)		35–25 (h)	50–45 (h)		
Hardwoods [28]	25–18 (h)		40–24 (h)	55–40 (h)		

Table 3 – Yield of lignin, holocellulose, hemicelluloses and cellulose from fern. Extraction methods used: (a) (LIG), (b) (ADL), (c) (ADLB), (d) (HOLO), (e) (HOLO- α), (f) (α), (g) (NDFB-ADFB), (h) (ADFB-ADLB), (i) unknown, (j) Weende, (k) NDF-ADF and (l) NDF-ADL.

Method	Lignin (wt% dry)	Holocellulose (wt% dry)	Calculated hemicelluloses (wt% dry)	α -cellulose (wt% dry)	Extractibles (wt% dry)	Dry matter (%)	Ash (wt% dry)
This work: “wood-industry” method	35 \pm 2 (a)	68 \pm 5(d)	34 \pm 9(e)	34 \pm 4 (f)	3 \pm 2	91	
“Food-industry” method	22 \pm 5(c)		4 \pm 2(g)	26 \pm 10 (h)		91	
“Food-industry” method	18 \pm 3(b)		13 \pm 2(k)	37 \pm 6 (j) 35 \pm 9 (l)			
Warm-season grasses [29]	19–18 (i)		33–24 (i)	43–35 (i)			8–2
Cool-season grasses [29]	14 (i)		36–25 (i)	35–24 (i)			11–6

biomass (Table 2), different values are obtained when the “food-industry” method is employed (25 wt% vs. 16 wt%). This method is similar to our Klason lignin (LIG) extraction process, except a final step of 1 h of calcination at 550 °C.

In Table 3, a large difference is observed between our results and the others, 35 wt% of lignin in fern against 22 wt% and 18 wt% for the ADLB and the ADL results, respectively. The content of lignin found in the fern, known to be a poorly lignified material, is too important to be realistic. Most of the methods used for the lignin determination are based on the following definition: lignin represents the material “insoluble in acid after the hydrolysis of the carbohydrate fraction”. This assumption is invalid for many biomass samples, particularly herbaceous materials for which proteins can condense with lignin. The resulted compounds are also insoluble and therefore assimilated to as lignin. A recent study dealing with the determination of lignin in straw of herbaceous crops highlighted the link between lignin structures and fractionation processes for major components [31]. The main obstacle for applying this method to herbaceous crops biomass stands in the incomplete separation of lignin–carbohydrates complexes. Indeed, lignin is always associated with carbohydrates via covalent bonds. Because of the chemical nature of lignin, it is practically impossible to extract lignin in pure form. Additionally, some extractives being insoluble in acid could precipitate, and could be taken into account in the lignin amount. In this case, the food industry methods are therefore the most

adapted. For the following study, only the ADLB values were considered.

3.1.2.3. α -Cellulose determination. The results obtained with the different wood biomass extraction methods are close: 43 wt% (this work) and 41 wt% (ADFB–LIGB). Concerning the fern biomass, the conventional method using the difference between ADFB and LIGB allows obtaining α -cellulose content: 26 \pm 10 wt%, which is close to the two others α -cellulose contents, 34 \pm 4 wt% and 37 \pm 6 wt%, determined by a basic hydrolysis (α -extraction) and the Weende method, respectively. Large uncertainty in the α -cellulose determination makes the results difficult to discuss.

3.1.2.4. Hemicelluloses content. Results obtained from the three different conventional methods for the determination of hemicelluloses content differ. Hemicelluloses content from this study (28 wt%) is close to the classical hemicelluloses values found for the wood, while the value of 9 wt% obtained by the food industry method is much lower (Table 2). Equally, the hemicelluloses contents of fern are not the same according to the considered method (4 wt% compared to 13 wt% with the food industry methods). This can be explained by the additional calcination step used in the method “NDFB–ADFB”. Once again, these values are lower than the hemicelluloses contents obtained with our “wood-industry” method, (i.e. 34 wt% (Table 3)). The most common isolation method for hemicelluloses is the alkali

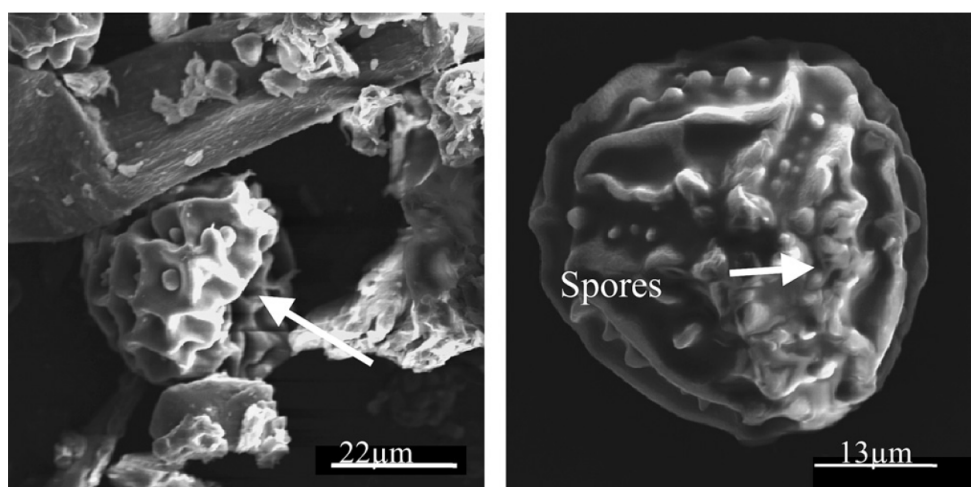


Fig. 2 – SEM pictures of the fern lignocellulosic materials.

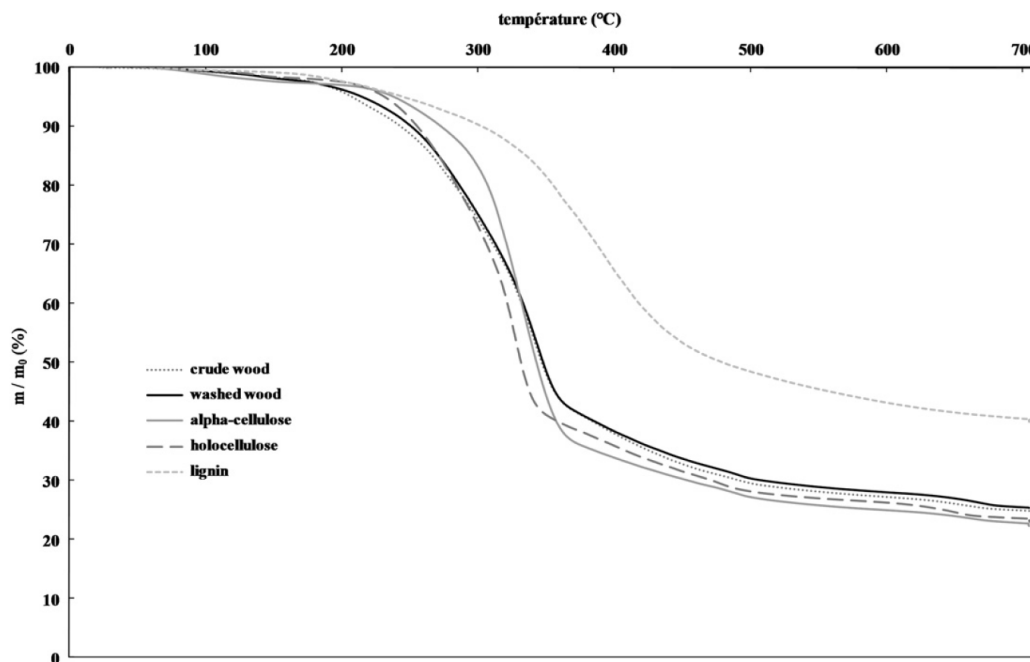


Fig. 3 – TGA curves of the crude, the washed wood and the macrocomponents extracted from the washed wood under an argon flow.

extraction of holocellulose used in this work. Apparently, the acid detergent solution used for determining the Acid Detergent Fibre content does not remove completely hemicelluloses to the “ADF material” and is, therefore, unsuitable for this process.

3.1.3. Scanning electron microscopy

SEM images presented in Fig. 2 reveal a main difference between the extracted materials (holocellulose, α -cellulose and lignin) issued from wood biomass and those from fern. In the latter, pollen beads and spores can be seen (lignin, holocellulose and

α -cellulose), making the extraction difficult whatever the considered determination method. Indeed, their presence could change the macromolecule contents determined for fern biomass by the chemical methods. As indicated in the previous paragraph (3.1.2.2), the “Klason lignin” is known as the insoluble component in a concentrated sulphuric acid solution. The presence of the pollen beads and spores - also insoluble - can induce errors.

Through this first part, dealing with the determination of two biomass compositions - poplar wood and fern, we have pointed out the large uncertainty inherent to standard

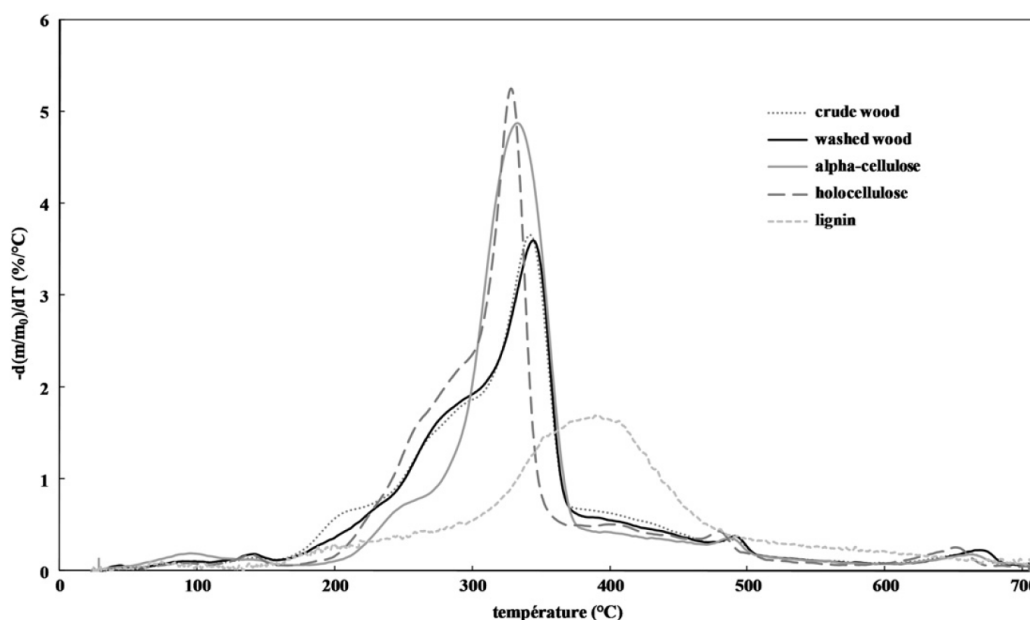


Fig. 4 – DTG curves of the crude and washed wood, and the macromolecules extracted from the washed wood.

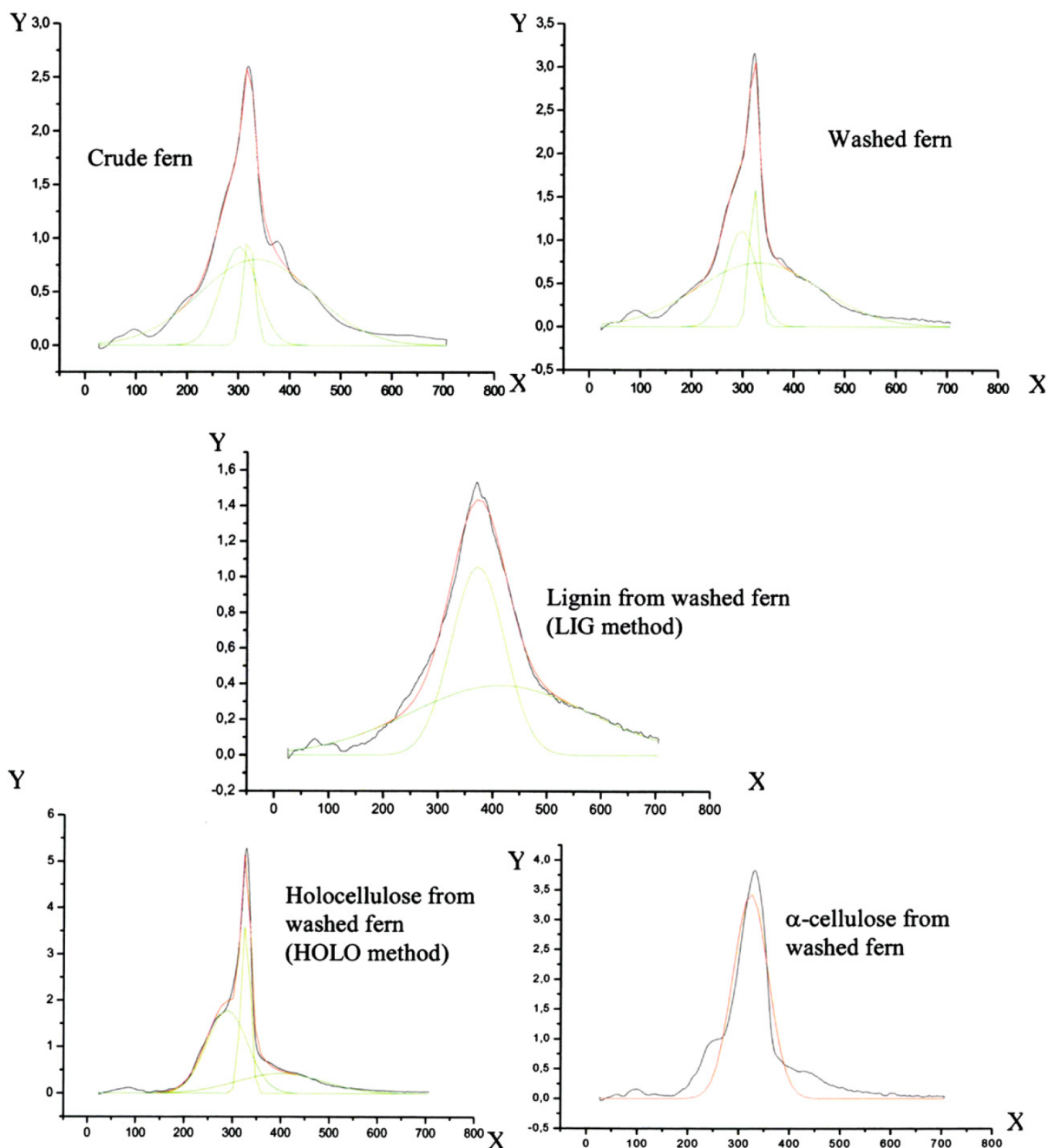


Fig. 5 – Deconvolution computation of DTG curves from Origin software with X: Temperature ($^{\circ}\text{C}$) and Y: DTG- $d(m/m_0)/dt$ ($\%/^{\circ}\text{C}$). Black = experimental DTG; Green = calculated peaks from the deconvolution computation with Origin software; Red = simulated DTG curve. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

methods. Also have we demonstrated the importance of choosing the right chemical method to determine the lignocellulosic composition depending on the considered biomass type.

In the next part of this paper, the “extractives-free” biomass (called the “washed biomass”) and the crude biomass were analyzed by thermogravimetric analysis as an alternative method to determine the amounts of hemicelluloses and α -cellulose. This was achieved through the plot of calibration curves (DTG area as a function of weight).

3.2. Thermogravimetric analysis

3.2.1. Thermogram

In first approximation, most lignocellulosic materials can be regarded as a mixture of 40–80 wt% of cellulose, 15–30 wt% of hemicelluloses and 10–25 wt% of lignin. TGA was used to determine the amount of lignin, cellulose and hemicelluloses in the biomass. TGA analyses were carried out on two different biomasses: fern and wood, the latter only being presented for sake of clarity.

Table 4 – Determination by deconvolution of the areas from the DTG curves for each component (Weight: initial dry weight introduced in TGA apparatus; Area is obtained by the deconvolution computation; ratio = Area/Weight (a.u. mg⁻¹) for the fern *Pteris vittata* L.).

	Weight (mg)	Area (au)	Ratio
Lignin (from the crude fern)	1.36	180	132 ± 43
(From the washed fern)	1.64	200	122 ± 40
(Obtained with LIG method)	4.07	290	72 ± 10
Holocellulose (from the crude fern)	4.80	125	26 ± 9
(From the washed fern)	5.34	110	21 ± 8
(Obtained with HOLO method)	7.86	190	24 ± 4
Hemicelluloses (from the crude fern)	2.60	80	31 ± 11
(From the washed fern)	3.01	60	20 ± 9
(Obtained with HOLO- α)	3.93	110	28 ± 4
α -cellulose (from the crude fern)	2.30	70	30 ± 11
(From the washed fern)	2.67	40	15 ± 7
(Obtained with a method)	8.45	300	36 ± 5

Thermogravimetric tests in inert atmosphere (Ar) were achieved to evaluate the pyrolytic behaviour of the biomass. The TGA curves obtained in Ar are plotted in Fig. 3. They show that the devolatilization process starts at 150 °C and the maximum weight loss occurs in the range 300–350 °C. Above 370 °C, an abrupt change in the slope of the TGA occurs leading to a slower weight loss in the temperature range 370–400 °C (Fig. 3). The evaluation of the weight loss of the samples between 120 °C, the end of moisture evaporation, and 550 °C, indicates that more than 70 wt% of the volatile matter was released in this interval.

3.2.2. Differential thermogravimetric spectra

Fig. 4 shows the differential thermogravimetric (DTG) curves obtained from the crude and the washed wood, and the macrocomponents: α -cellulose, holocellulose and lignin.

The crude and washed biomass curves present three main peaks from the hemicelluloses degradation in the temperature range 200–300 °C, the others shoulders in the 250–350 °C

Table 5 – Determination by deconvolution of the areas from the DTG curves for each component (Weight: initial dry weight introduced in TGA apparatus; Area is obtained by the deconvolution computation; ratio = Area/Weight (a.u. mg⁻¹) for the poplar wood *Populus nigra* L.).

	Weight (mg)	Area (au)	Ratio
Lignin (from the crude wood)	2.35	180	77 ± 26
(From the washed wood)	2.67	170	64 ± 21
(Obtained with LIG method)	8.56	302	35 ± 5
Holocellulose (from the crude wood)	5.56	184	33 ± 11
(From the washed wood)	6.69	213	32 ± 11
(Obtained with HOLO method)	8.64	259	30 ± 4
Hemicelluloses (from the crude wood)	2.19	104	47 ± 15
(From the washed wood)	2.76	133	48 ± 16
(Obtained with HOLO- α)	3.20	159	50 ± 8
α -cellulose (from the crude wood)	3.36	80	24 ± 8
(From the washed wood)	3.92	82	20 ± 7
(From the cotton)	6.52	230	35 ± 6
(Obtained with a method)	8.73	291	33 ± 5

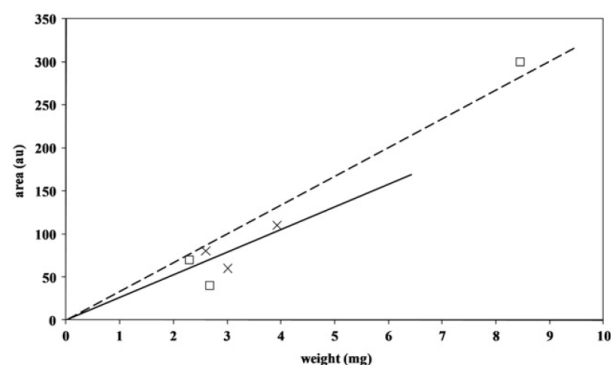


Fig. 6 – Calibration curves of α -cellulose (\square) and hemicelluloses (\times) for the fern sample - - -: linear regression for α -cellulose —: linear regression for hemicelluloses.

and 200–500 °C temperature ranges correspond to α -cellulose and lignin, respectively. The relative intensities of the peaks can be related to the global quantities of hemicelluloses, cellulose and lignin present in the wood.

In the same conditions, the holocellulose, α -cellulose and lignin amounts obtained by the standard methods for fern and wood were analyzed by TGA. The DTG curve of holocellulose shows the presence of hemicelluloses and α -cellulose in high proportions. Additionally, the presence of a shoulder at higher temperature corresponds to traces of lignin in the sample, despite of the sodium acetate and sodium chlorite treatments (LIG method). The same holocellulose was treated by a NaOH solution (HOLO method) and the DTG curve of α -cellulose indicates the presence of a larger peak corresponding to high concentrations of this latter. However, the presence of a peak in the temperature range 200–300 °C confirms that hemicelluloses have not been fully removed from the sample. The DTG of lignin obtained from the washed biomass after an acid hydrolysis confirmed an efficient extraction. Indeed, the lignin is known to decompose slowly over a broad temperature range, resulting in the flat tailing section of the DTG curve.

It can be pointed out that with the knowledge of the initial masses introduced in the thermogravimetric equipment, the relative intensity of the curves could be compared.

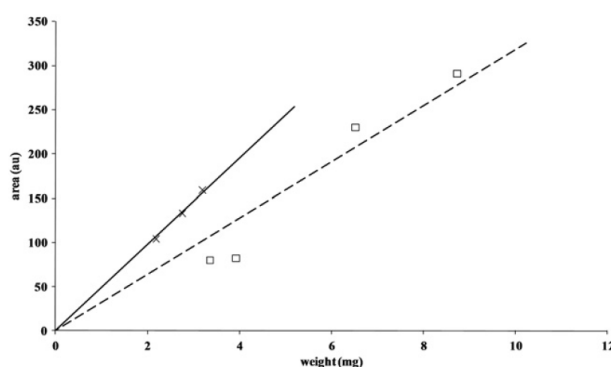


Fig. 7 – Calibration curves of α -cellulose (\square) and hemicelluloses (\times) for the wood sample. - - -: linear regression for α -cellulose —: linear regression for hemicelluloses.

3.2.3. Deconvolution of DTG curves

Fig. 5 shows the DTG curves for each product: the crude fern, the washed fern, the holocellulose, the α -cellulose, and the lignin extracted from the fern. The Origin software was used to carry out the deconvolution computation of the DTG curves.

Three peaks corresponding to hemicelluloses (1), α -cellulose (2) and lignin (3) were observed in the crude and washed ferns. In the previous paragraph, we highlighted the presence of some residual lignin in the holocellulose material. These three peaks were determined from the deconvolution treatment in order to have the true hemicelluloses and α -cellulose areas. For the α -cellulose component, the main peak was distinguishable, whereas for the lignin component the plot of two calculated Gaussian peaks was necessary to obtain the total integrated area.

First, the conventional wet methods allow us to obtain separately the amount of the different macroelements from some biomasses: holocellulose, α -cellulose and lignin. Then, the crude and “extractive-free” biomasses were analyzed by TGA. Tables 4 and 5 indicate the weight and the values of the integrated area obtained for each component after the deconvolution of the DTG curves. The last column is the ratio between the area (arbitrary unit) and the dry initial weight (mg). This ratio illustrates the correlation between weight and integrated area and whether it is meaningful. Errors were quantified from conventional methods ($\Delta\% = 20\%$): the initial weight introduced in TGA ($\Delta m = 0.1$ mg), the area after the deconvolution ($\Delta D = 11\%$), and the dry matter determination ($\Delta MS = 0.5\%$). The ratios were compared in order to know whether we obtained a good agreement between i) the direct TGA analysis of the crude and washed ferns and ii) the TGA analysis of each extracted macrocomponents obtained by wet standard methods. A similar procedure was conducted to determine the possible correlation in the case of the poplar wood biomass.

Although a good agreement is obtained for the calculation of the holocellulose and the α -cellulose amounts, as well as for the amount of hemicelluloses obtained by difference, the calculation of the lignin quantity does not lead to satisfactory correlation. The reproducibility of the results has not been enhanced despite an extraction step performed before the determination of macromolecule amounts.

Two calibration curves were plotted in order to determine easily and quickly the hemicellulose and α -cellulose contents in others biomass samples (Figs. 6 and 7).

Note that the calibration curves are obtained with a linear regression, with a reasonable correlation coefficient. However, it appears that the correlation is unsatisfactory for the determination of the hemicellulose content in the case of the fern sample. The hemicellulose content is obtained by subtracting

Table 6 – α -cellulose content in the cellulose pulps coming from “pin maritime” by (1) R10 method and (2) from the calibration curves of the fern and wood samples.

Sample	α -cellulose content (wt% dry) (1)	Wood (wt% dry) (2)	Fern (wt% dry) (2)
110106	87.6	79 \pm 7	74 \pm 6
5092	90.3	97 \pm 7	91 \pm 6
5094	92.8	96 \pm 8	91 \pm 7
5096	93.6	99 \pm 8	93 \pm 7

Table 7 – Hemicelluloses content in the cellulose pulps coming from “pin maritime” by (1) 100-R18 method and (2) from the calibration curves of the fern and wood samples.

Sample	Hemicellulose content (wt% dry) (1)	Wood (wt% dry) (2)	Fern (wt% dry) (2)
110106	11.7	8 \pm 4	17 \pm 10
5092	7	6 \pm 3	13 \pm 7
5094	4.7	6 \pm 4	13 \pm 9
5096	3.6	5 \pm 4	10 \pm 9

holocellulose to α -cellulose deconvolution results, inducing an additional error in the determination of hemicelluloses content.

Cellulose pulps were used as model system to validate our method. Four different samples, with very precisely known content of hemicelluloses and in α -cellulose were analyzed by TGA. Once the deconvolution computation was achieved, the corresponding weights were obtained from the calibration curves (Figs. 6 and 7). Then, they were divided by the initial dry weight introduced in the thermogravimetric experimental setup. It is worth noticing that results (Tables 6 and 7) differ considerably using the calibration curves of the wood or fern, particularly in the case of hemicelluloses content. The results show that the best agreement between the hemicellulose obtained by the extraction of pulps with 18% of NaOH (R18 method) and the “thermogravimetric” determination is obtained when using the wood calibration curve. These cellulose pulps were extracted from the “pin maritime”, a wood biomass, making this result coherent. In the case of the α -cellulose determination, the variation obtained using both calibration curves makes difficult the choice of the best calibration curve.

The correlations for the lignin component are not as good as the hemicelluloses and α -cellulose ones because of the use of the “Klason lignin” method, which differs from the real amount of the lignin in a biomass sample. Indeed, condensation reactions were observed during the extraction procedure explaining this difference [32].

Small deviation for the values of α -cellulose (87.6–93.6 wt%) and hemicelluloses (3.6–11.7 wt%) values as well as for their precision (high purity cellulose pulps) were not suitable to highlight the efficiency of the thermogravimetric determination presented in this study. Nevertheless, the fast thermal determinations of the α -cellulose and hemicelluloses contents seem to be well adapted to crude biomass sample compared with the high standard deviations induced by classical wet methods.

4. Conclusions

Numerous fractionation methods exist for the separation of the macromolecules contained in biomass: lignin, holocellulose and α -cellulose. In this study, we have reported the variations inherent to determination of their amount according to a specific extraction method. The lignin content in an herbaceous material such as the fern *P. vittata* L. was determined more precisely using the “food-processing industry” methods. However, the amount of hemicelluloses in the fern and wood samples is not well known because these methods minimized

its value. Therefore, the alkaline extraction procedure is recommended for this particular case.

The second main result of this work is the use of the thermogravimetric analysis in order to determine the α -cellulose and hemicellulose amounts in a biomass sample. Successful correlations between the component contents issued from chemical extraction methods and thermogravimetric analyses have been obtained. The thermogravimetric method allows for accurately determining values of the hemicelluloses and α -cellulose contents in cellulose pulps. However, the successful TGA methods cannot be extended to the lignin content because of important deviations in the correlation curves. Through this alternative method, which is faster, easier to implement, and less cost effective than existing wet chemical techniques, it is possible to determine with comparable or enhanced accuracy the hemicelluloses and α -cellulose contents of biomass samples.

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