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On the chemical composition and pyrolytic behavior of hybrid poplar energy crops from northern Spain

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Abstract

Short Rotation Woody Coppices (SRWCs) where several tree species and clones grown on marginal land typically over 3–10 year cycles have been recognized as providers of sustainable energy and as feedstocks for producing other fuels and chemicals. A thorough physical and chemical characterization is crucial for understanding and optimizing harvesting and production strategies. Accordingly, this study focuses on the evaluation of chemical and thermochemical features of three parts of harvested shoots (base and middle of the shoot, and branches) of selected hybrid poplars of short rotation -AF2, Beaupré and I214 of 5, 9 and 8 years-old, respectively-. Results show a decrease in the ash content from the top to the base of each species with ash levels always around or below 1 wt%, and at the same time a decrease in high heating value -HHV-. The differences in HHV between the different parts of the hybrid poplars are in good agreement with results obtained from FTIR and thermogravimetric patterns.

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Keywords: Bioenergy; Chemical composition; FTIR spectroscopy; Pyrolysis

1. Introduction

At the beginning of this decade, the government of Spain came to an agreement with the European Commission regarding the closure of the unproductive coal mines [1]. Asturias is, alongside Castilla y León and Aragón, the region that has been most affected by the end of coal mining. As a consequence of the intense mining activity in Asturias in the past, large areas of land needed to be recovered. This land now consisted of forests, pastures and regenerated landscapes. From 2009 to 2012, forest repopulation, with more than 150 000 trees planted, led

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to a forest covered surface area of 3854 ha. Of this area, 1565 ha could be used for growing energy crops in Short Rotation Woody Coppices (SRWCs) [2]. Initiatives of this type are being undertaken as part of a series of experimental trials established on abandoned mining land in Asturias [3]. These experiments, established on the basis of a randomized complete block design, involve several species and clones, including the most forest productive poplars, selected for this study due to the fact that it adapts itself readily to extreme conditions such as contaminated and nutrient-impoverted soils [3,4]. The SRWCs, especially on degraded sites, cultivated with the aim of producing high biomass yields in a short period of time (3–10 years) represents a potentially reliable means of reactivating the energy sector and gradually replacing the extraction of fossil fuels in the region.

The aim of this work is to evaluate the relationship between chemical composition and pyrolysis behavior of woody biomass using hybrid poplar energy crops. Three poplar clones for short rotation – AF2, Beaupré and I214 – were collected from the experimental trials for woody biomass production. The present study includes a proximate analysis, an ultimate analysis and a heating value assessment of the three clone varieties, together with the evaluation of the functional groups by means of infrared spectroscopy and of the evolution of volatile matter under pyrolysis conditions by thermogravimetry. The samples were collected and analyzed from three different parts of each harvested shoot (base and middle of the shoot, and branches). This study will also provide information about the evolution of the most prominent chemical and thermal features during the growth process.

2. Materials and methods

2.1. Woody biomass

The lignocellulosic biomass used in this study was obtained during harvesting operations on a short rotation plantation of a former opencast coal mine located at El Cantil-Asturias in northern Spain. The tree species investigated were three hybrid poplars that are currently being employed on short-rotation coppice (SRC) plantations as bioenergy feedstocks: AF2 (*Populus nigra* x *Populus deltoides*), Beaupré (*Populus deltoides* x *Populus trichocarpa*) and I214 (*Populus nigra* x *Populus deltoides*). AF2 was harvested and chopped up using a whole tree harvester 5 years after planting, whereas the growth cycles of Beaupré and I214 were 9 and 8 years, respectively. The samples were classified into three different parts of the harvested shoot: base and middle of the shoot, and branches from the top. The cut sections were dried by means of forced air circulation at 35 °C for 48 h to reduce the moisture content by up to 3.9–5.6 wt% and then crushed and sieved so as to obtain particle size fractions between 0.212 and 1 mm. The particle morphology of the ground samples was short and splinter-like. Subsamples retained prior to crushing were used as a yardstick to determine the proportion of wood and bark in each piece.

2.2. Chemical and thermochemical characterization

Proximate analyses were performed to classify the fuels in terms of their thermochemical composition on the basis of moisture, volatile matter and ash contents in accordance with the ISO 17246:2010 standard procedure. The ash-free carbon-rich solid remaining after drying and devolatilization (fixed carbon) was calculated by subtracting the percentages of moisture, ash, and volatile matter. Elemental analysis was consisted of C, H, N, S and O. The oxygen content was calculated from the mass balance. The gross calorific value or high heating value (HHV) was experimentally determined by using an adiabatic bomb calorimeter.

2.3. Fourier transform infrared (FTIR) spectroscopy

Fourier-Transform infrared (FTIR) spectra were recorded on a Nicolet IR 8700 spectrometer fitted with a mercury–cadmium telluride detector (MCT/A) operating at sub-ambient temperature and a Smart Collector diffuse reflectance (DRIFT) accessory. Spectra of the dried samples were obtained by co-adding 64 scans at a resolution of 4 cm⁻¹ in the mid IR region 4000–650 cm⁻¹. Several FTIR indices derived from the maximum intensity (I) of selected absorption bands were used to assess the changes in the chemical structure of the different biomasses.

2.4. Thermogravimetric analysis

The samples were pyrolyzed using a TGA/DSC1 Star System Mettler Toledo thermoanalyzer. Samples of about 5 mg with a particle size of <212 μm were evenly distributed on an open platinum pan and, then, heated from

ambient temperature up to 800 °C at a rate of 10 °C/min. The final temperature was maintained for 2 min. Nitrogen was supplied as an inert and sweep gas at a flow rate of 75 ml/min.

3. Results and discussion

Table 1 summarizes some of the characteristics of the pieces of wood collected from the SRWC plantation. The pieces selected from each hybrid poplar and from different parts of the tree contain wood and bark without any foliage or roots. As the characteristics of the woody biomass determine its commercial value and use, it is necessary to control the characteristics of the whole tree, e.g. the proportion of wood to bark, and the chemical and physical characteristics of the stem-branch wood. Given that the samples studied contain wood and bark, a cut-up subfraction of three sections was employed to determine the proportions of these constituents. The amount of bark on each hybrid poplar varies from the base of the shoot to the branches at the top. The highest bark content is to be found in the branches at the top and it is significantly greater than the levels of bark in the middle and base sections of the tree, except for the AF2 species where the quantities of bark at the top and in the middle of the tree are similar. The bark content in weight percent varies within a very narrow range (20–22 wt%) in the upper branches. The lowest bark level is at the base (11–15 wt%), while in the shoot-middle the levels are intermediate. In contrast, in the case of AF2 most of the bark is more evenly distributed around the tree than in the poplars Beaupré and I214. The average thickness of the bark correlates with the average diameter of the cut sections and varies according to its position in the tree and the species of tree.

Table 1. Some anatomical features of the pieces of wood from the hybrid poplars.

Genotype	AF2			Beaupré			I214		
Taxon	<i>P. x canadensis</i>			<i>P. x generosa</i>			<i>P. x canadensis</i>		
Rotation cycle	2			1			1		
Age in years	5			9			8		
Tree part	Top	Middle	Base	Top	Middle	Base	Top	Middle	Base
Total moisture [wt%]	53	56	51	26	55	49	24	60	44
Bark [wt%]	22.3	20.6	14.9	19.9	11.9	11.8	22.3	14.1	11.5
Bark thickness [mm]	1.19	3.18	3.87	0.82	1.40	2.15	1.04	1.80	4.56
Wood diameter [mm]	24.2	55.6	89.3	23.0	41.8	56.0	25.3	69.3	110

The green pieces of wood contain a very large amount of water which is concentrated in the pores or vessels of the wood. The water content varies widely from as little as 24–26 wt% at the top of Beaupré and I214 to 44–60 wt% in the other parts of the tree (Table 1). The as-received pieces were air-conditioned to prevent any alteration of their properties, to facilitate the grinding process and to perform the subsequent analysis.

3.1. Intrinsic characteristics

Wood is a natural composite material that contains three carbon-based biopolymers in its cell-wall structure (cellulose, hemicellulose and lignin) together with bound water, small amounts of inorganic minerals (ash-forming compounds) and several classes of compounds that can be extracted from the wood using solvents (extractives). Woody biomass is, therefore, a heterogeneous material and its intrinsic characteristics are highly variable and have an effect on the economic and environmental performance of thermochemical conversion processes used to produce fuels, powder and chemicals. The thermal application is dependent on chemical composition and its energy content.

Table 2 shows the intrinsic characteristics of biomasses in terms of their proximate and elemental compositions as well as their high and low heating values (HHV and LHV, respectively). Hybrid poplars are characterized by their high VM and oxygen contents as well as their low C, H, S and ash concentrations compared to fossil fuels. Only minor differences can be observed between one sample and another and the elemental balances are determined by the chemical structure of the lignocellulosic components. The C, H and O account for between 98 and 99% of the wood sample, while N and S are present as minor elements. The N content that contributes significantly to NO_x emission is always less than 1 wt% and has a clear decreasing evolution from the top to the base of the trees. Among the poplars, Beaupré is the hybrid with lowest N content. The quantity of S is low (<0.03 wt%) and no

Table 2. Main characteristics of hybrid poplars.

	AF2			Beaupré			I214		
	Top	Middle	Base	Top	Middle	Base	Top	Middle	Base
Moisture (wt%)	4.73	4.48	4.07	4.53	5.00	4.14	5.74	4.87	3.94
Ash (wt% db)	1.03	0.87	0.85	1.06	0.62	0.68	1.14	0.75	0.51
Volatile matter – VM- (wt% db)	80.85	81.00	81.82	81.88	83.78	83.72	80.95	81.52	82.06
Fixed Carbon – FC- (%)	18.12	18.13	17.33	17.06	15.60	15.60	17.91	17.73	17.43
C (wt% db)	50.31	50.53	49.72	49.32	49.59	49.13	50.15	50.24	49.75
H (wt% db)	5.98	5.97	6.04	6.14	5.97	6.01	6.08	6.02	6.01
N (wt% db)	0.65	0.42	0.35	0.47	0.33	0.30	0.77	0.45	0.35
S (wt% db)	0.03	0.02	0.01	0.02	0.01	0.01	0.02	0.02	0.01
Odif (wt% db)	42.00	42.19	43.03	42.99	43.48	43.87	41.84	42.52	43.37
HHV (MJ/kg)	19.96	19.89	19.74	19.79	19.64	19.53	19.96	19.93	19.65
LHV (MJ/kg)	18.74	18.67	18.50	18.53	18.42	18.30	18.72	18.70	18.42

distinctive trends are apparent for this element. Also of interest is the VM content which shows the opposite trend to FC. It is high in the 80%–84% range and, so plays a very important role in promoting the combustion reaction.

As can be seen from Table 2 the similarity of the chemical and thermochemical compositions of the samples is related to the amount of heat energy contained in the wood and released during its combustion. The HHV of AF2 at the three tree sections, -top, middle and base-, are 19.96, 19.89 and 19.74 MJ/kg, respectively, decreasing from top to base. The other poplars exhibit the same trend, which is independent of age. The net calorific value or low heating value (LHV), -calculated from the HHV and the concentration of hydrogen at zero moisture-, also follows the same pattern. This means that the calorific value is negatively correlated with tree diameter, but positively correlated with tree height, and bark quantity when wood is evaluated as a potential fuel for obtaining heat energy. However, HHV differences between the three parts of the tree account for <1.5%. Another compositional parameter used to screen wood as a fuel feedstock is its ash content. The ash content is also correlated with tree diameter, height and bark quantity. In the case of the poplars, AF2 and I214, the ash content decreases slightly from top to base. It is well known that the quality of wood as a fuel decreases as the amount of ash increases. However, in all cases the amount of ash at the three tree heights analyzed is very low (around and below 1 wt%).

The HHV of wood is a crucial parameter for determining its potential use as energy source. Several mathematical models have been developed to predict the HHV as an alternative to direct experimental assessment by using an adiabatic bomb calorimeter. In the present study, the HHV were also calculated by using the Dulong–Berthelot model developed to estimate the HHV of coal on the basis of the elemental analysis and modified by Channiwalwa and Parikh [5] to evaluate other types of fuels (solid, liquid and gas). In all samples, the calculated values are in close agreement with the experimental ones with <2% error.

3.2. Structural and thermogravimetric analysis

In the DRIFT spectra of the hybrid poplars recorded at the three tree heights selected for analysis (top, middle and base) a series of common absorption bands dominate the spectra and the absorption bands differ only slightly in position and intensity. The infrared spectra of the woods can be categorized into three main regions: (1) the stretching vibration of hydrogen bonded O–H located around 3420 cm^{-1} as a strong and broad band; (2) the stretching vibrations of the C–H bonds in methylene and methyl groups with a prominent band at around 2920 cm^{-1} and unresolved bands at low wavenumbers; and (3) the fingerprint region (1800 to 650 cm^{-1}) where the absorption bands represent functional groups of polysaccharides and lignin [6,7]. The focus of this work is to use FTIR indices to reflect the amounts of specific functional groups of lignin and polysaccharides and to correlate them with the thermochemical characteristics of the woody biomass studied.

The most significant correlations were found between the high heating value (HHV) and two FTIR indices, I_{1507}/I_{898} and I_{1507}/I_{2920} , which are defined as the ratio between the heights of known marker bands of lignin (C = C aromatic stretching vibrations at 1507 cm^{-1}) and cellulose (C–H stretching of methylene groups at 2920 cm^{-1} and C-H out-of-plane deformation of glucose rings in cellulose at 898 cm^{-1}). Extractives also contribute to the

intensity of the bands at 2920, 2850, and 1510 cm^{-1} [8]. Consequently, the FTIR indices defined give information about the C = C of aromatic systems in lignin, extractive compounds and cellulose.

Although some deviations from linearity occur and the differences in HHV are not great, the increase in the specific functional groups of lignin relative to carbohydrates evidenced by the increase in the I_{1507}/I_{898} and I_{1507}/I_{2920} indices, seems to be closely linked to an increase in HHV. As an example, Fig. 1 shows the relationship between the experimental HHV (expressed in J/g) and the I_{1507}/I_{898} index with a correlation coefficient of 0.884. The lignin content of lignocellulosic fuels is closely correlated with HHV, but other factors that have been shown to influence the HHV such as moisture, ash and extractive compounds [5,9,10] have not been considered in this study. Although the limitations of the present data are apparent from the scattering diagram, i.e. the reduced number of samples and the differences in age of the hybrid poplars, the HHV estimated are in reasonable agreement with the experimental values, with differences ranging from 3 to 120 J/g.

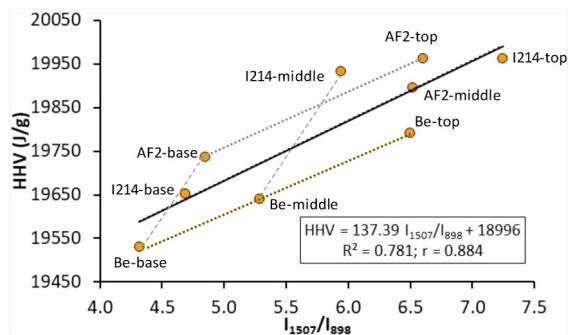


Fig. 1. Relationship between the HHV and the I_{1507}/I_{898} index-ratio of heights of known marker bands of lignin and some types of extractives (1507 cm^{-1}) and cellulose (898 cm^{-1}).

It is important to point out that the y-intercept at zero-value of the I_{1507}/I_{898} index, or in other words the absence of lignin and aromatic extractives, has an HHV of 18 996 J/g which is consistent with the HHV of 18 608 J/g for cellulose and hemicellulose [10]. This figure brings to light four other important points. The first point is the classification of the three samples from the base of the trees as a nearly straight isoline with an increasing order of the two variables (HHV and I_{1507}/I_{898}): Beaupré < I214 < AF2. The second point is the intermediate isoline representing the samples with a longer growth cycle, 9 and 8 years for Beaupré and I214, respectively. The third point is the linearity of Beaupré from the base to the top. Finally, the right region of the graph shows the three species at the top and the AF2 middle. AF2 is the youngest tree (5 years growth cycle) and the middle and top sections show a similar HHV and a similar quantity of components contributing to energy production.

FTIR spectroscopy, generally recognized as attractive technique for biomass, provided useful and discriminatory information on the organic matter and the energy content of the different parts of the hybrid poplars. However, further research is needed to improve its potential for estimating the HHV and other thermochemical properties.

The pyrolysis behavior of the samples was assessed by thermogravimetry. All the samples studied exhibit a typical DTG profile for the thermal decomposition of lignocellulosic biomass [6,11]. The DTG curves show the occurrence of different overlapping processes (Fig. 2). The main peak which is assigned to the decomposition of

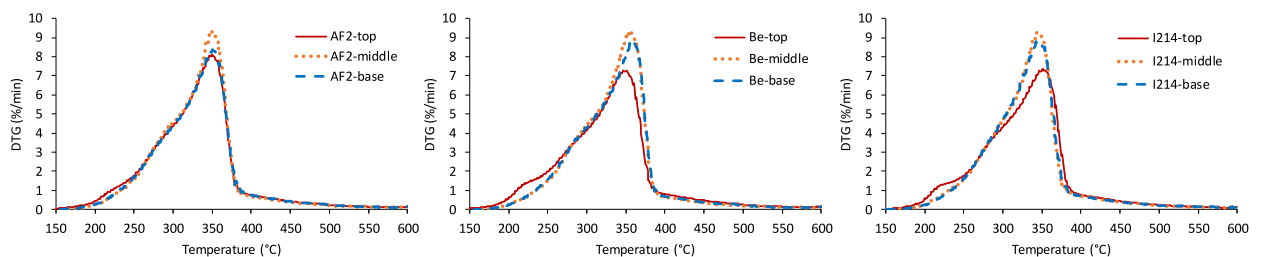


Fig. 2. DTG profiles in the temperature interval 150–600 °C of the different parts of hybrid poplars.

cellulose shows a typical shoulder and tail attributable to hemicellulose and lignin, respectively. Fig. 2 shows the DTG curves for the three different parts of each poplar. In this figure, it can be seen that the samples from the middle and base of the tree have similar profiles, while that corresponding to the branches at the top is slightly different. Samples collected from the top exhibit a distinctive shoulder at a much low temperature and starting decomposition at near 150 °C which might be attributable to extractives and lignin with decreasing complexity of molecular structure and less thermally stable. If this is the case, the compounds of this fraction which contain C = C aromatic rings in their structure will increase the HHV and the value of the I_{1507}/I_{898} index compared to the base and center of the poplars.

4. Conclusions

Only minor differences in the chemical and thermochemical characteristics of the different parts of three hybrid poplars collected from a SRWC plantation were found. The differences in ash content and high heating value, however, were appreciable. The FTIR index (I_{1507}/I_{898}) appears to be a good indicator of the wood components that contribute to the energy potential of the different species and parts of each hybrid poplar. The observations made from the FTIR indices were confirmed by thermogravimetry. Thus, DRIFT spectroscopy and thermogravimetry appear to be suitable techniques for acquiring a rapid overview of the thermochemical dissimilarities between the top, middle and base of the tree and between poplar species.

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