COMPARATIVE THERMOGRAVIMETRY/MASS SPECTROMETRY STUDY OF WOODY RESIDUALS AND AN HERBACEOUS BIOMASS CROP USING PCA TECHNIQUES

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Abstract

The devolatilization behavior of pine and beech wood from carpentry residuals and an herbaceous product from an energy crop (artichoke thistle) was investigated by thermogravimetry/mass spectrometry (TG/MS). The effect of three pretreatments, hot-water washing, ethanol extraction and their combination were also studied. The results show that the thermal behavior of wood and thistle are still considerably different after the elimination of some of the inorganic components, however, the macromolecular components decompose at similar temperatures. Since we had a large number of samples and TG/MS data, we have employed principal component analysis (PCA) to help the evaluation of the results and the comparison of the samples.

Introduction

Ministers and Government Representatives from 154 countries gathered in Bonn[1] acknowledge that renewable energies combined with enhanced energy efficiency, can significantly contribute to sustainable development, providing access to energy, mitigating greenhouse gas emissions, reducing harmful air pollutants, thereby creating new economic opportunities, and enhancing energy security through cooperation and collaboration.

The increased exploitation of biomass materials different from the species usually investigated requires a better description of both the dynamics and the influence of the heterogeneities on biomass thermolysis. With a view of studying the influences of feedstock properties, special attention has been given to the effects of pretreatments on the kinetics. Several studies have evidenced the ability of pretreatments to separate merged peaks, displace reaction zones toward higher temperatures, decrease char yield and increase peak reaction rates[2]. At the time being the understanding of the effects of pretreatments remains largely qualitative. The various industrial applications (e.g. the production of charcoal, activated carbon and liquid fuels) require a clear understanding of the variations in the original composition and the effects of the pretreatments, since the yields and the composition, structure, and other properties of the products are highly influenced by the properties of the feedstock.

The thermal decomposition of cellulose, hemicellulose and lignin results in a high yield of low molecular mass compounds at low heating rate[3, 4], therefore the evolution profiles of these products are characteristic of the decomposition of wood components. The present work aims at the clarification of the thermal properties of important feedstocks that have not attracted yet sufficient attention in the biomass studies. The woody residuals of the carpentry industry remain largely unused and present a solid waste disposal problem. Thistle produced in an energy plantation is already a raw material of an electric power generation plant in Spain, although much remains to be learned about its thermochemical properties. The kinetic behavior of these biomasses under slow pyrolysis was already investigated in previous works[2]. The specific aim in the present work is to monitor the differences in the thermal behavior from the identification of main pyrolysis products. The range of the evaluated samples involves water-washed and ethanol-extracted samples as well as samples submitted to both water-washing and ethanol extraction. The purpose when submitting samples to those pre-treatments is to study the influences of inorganic ions and extractive materials on the pyrolytic behavior and reaction pathways. Principal components analysis (PCA) is applied to the interpretation of the experimental results.

Experimental procedure

The wood chips (pine and beech) were taken from Barcelona's region carpentry residuals, while the herbaceous sample (artichoke thistle) came from a specialized crop in the Spanish province of Soria. The TG/MS experiments were performed using a Perkin-Elmer TGS-2 thermobalance connected to a Hiden HAL quadrupole mass spectrometer, using argon purge gas. The sample mass was about 4 mg. The samples were heated from 20 °C to 900 °C at a heating rate of 20 °C min^{-1} in a platinum sample pan. The MS ion intensities were integrated within the temperature range of decomposition. The MS integrals of the most significant products – with good signal/noise ratios – have been applied as input data for the PCA calculation.

Results and discussion

TG/MS analysis

The resulting TG/DTG curves were first compared from a qualitative point of view (See Figure 1). The pretreatments had a much more pronounced effect on the thistle than on the wood due to the higher mineral matter and extractive content of the herbaceous sample, translated in degradation taking place over a narrower range and at lower temperatures. For all the samples the water-washing had a stronger effect on the decomposition than the extraction since in the later case only slighter displacement of the cellulose degradation toward higher temperatures is observed, indicating that the inorganic ions have higher effect on the decomposition than the extractives.

The evolution profiles of volatile products have been recorded by the mass spectrometer to gain a better understanding of the previously discussed differences. The TG/MS system could not detect some of the tar fraction due to condensation. Selected MS profiles of the untreated samples are shown in Figure 2. Since the MS intensities of various products have different magnitudes, they have been scaled to obtain comparable peak heights in the plots. The scaling factors for the individual species are the same. The identification of the ions is based on literature data and on chemical consideration of the wood structure[4, 5].

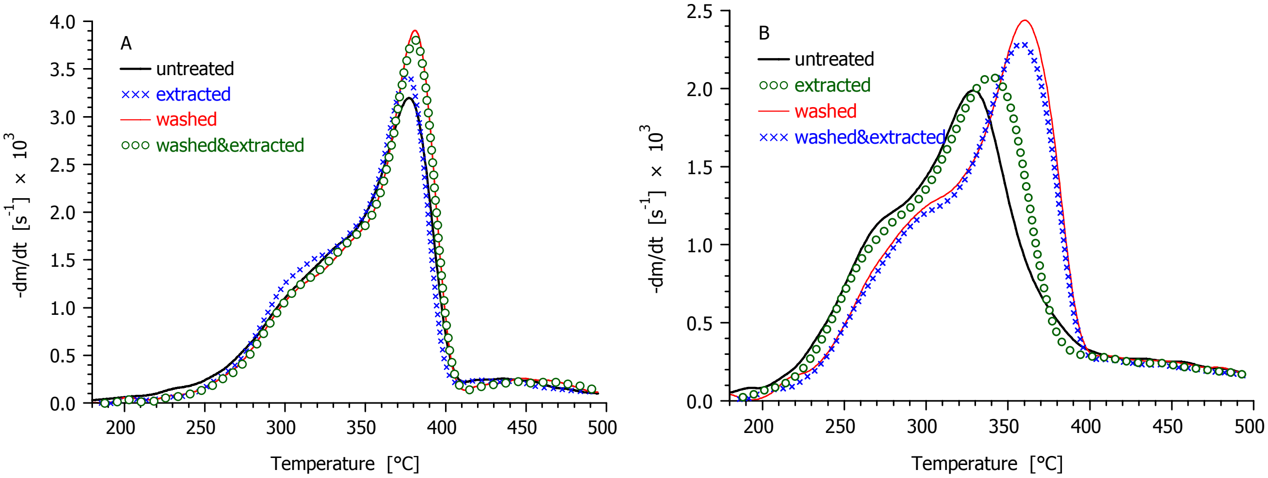

Figure 1. DTG curves of untreated and pretreated pine (A) and thistle (B) samples at 20°C/min.

Relatively large amounts of H_2O (m/z 18), CO (m/z 28) and CO_2 (m/z 44) are produced during the thermal decomposition of organic materials, owing to the large number of hydroxyl groups and oxygen atoms present in the natural polymers that make up the cell walls (cellulose, hemicellulose and lignin). The MS curves of carbon monoxide and carbon dioxide show differences between the different types of samples. Smaller portions of these gases are released after the major decomposition peaks of the polymers in the thistle sample. CO_2 and CO are formed around 500 °C with another remarkable evolution of this product between 600 and 700 °C. The origin of these peaks can be both organic matter and oxalate decomposition. The broad curve of CO above 600 °C can be attributed to the char formation reactions, when the residual O-functional groups are cleaved. It is confirmed by the evolution of H_2, which is also a product of this high-temperature charring reaction, as the methane evolution above 600°C decreases.

Methane (m/z 16) is formed in two main processes, much clearer observed during the decomposition of the woody samples. The first process at around 440 °C can mostly be attributed to the decomposition of lignin side groups[3]. Following this process, CH_4 is produced as a result of charring processes at temperatures 500 – 700 °C when profound degradation and rearrangement reactions occur. If one compares the methane curves of wood and thistle, it can be concluded that the charring reactions play a more significant role when the herbaceous sample is heated, which is consistent with its higher char yield.

In the panel B of Figure 2, the MS curves of some characteristic organic volatile products and fragments are shown. Formaldehyde (m/z 30) is a general product of hemicellulose, cellulose and lignin, hence its evolution profile resembles to the shape of the DTG curve. The m/z 31 ion is the main fragment ion of hydroxyacetaldehyde, which is a significant product of cellulose decomposition[4, 5]. Furthermore, m/z 31 corresponds to methanol, which is produced through the scission of the side-groups and end-groups of the polymeric cell wall constituents. The m/z 45 and 58 ions represent $COOH^+$ and $CH_3COCH_3^+$, respectively, which are released mainly from hemicellulose and cellulose. Hemicellulose produces relatively higher amount of acid products as the m/z 45 fragment ion indicates, which can be explained by the acetylate side groups of xylan polymer. Acetone originates mostly from cellulose as the evolution profile shows. Also, it is noteworthy that the decomposition of hemicellulose and cellulose are better separated in the wood than in the thistle, which is implied by the more distinct shoulder visible on the DTG and MS curves of wood around 300 ºC. In the case of thistle the MS evolution of the above exposed ions occurs in a lower temperature domain, indicating an unusual range of decomposition for cellulose.

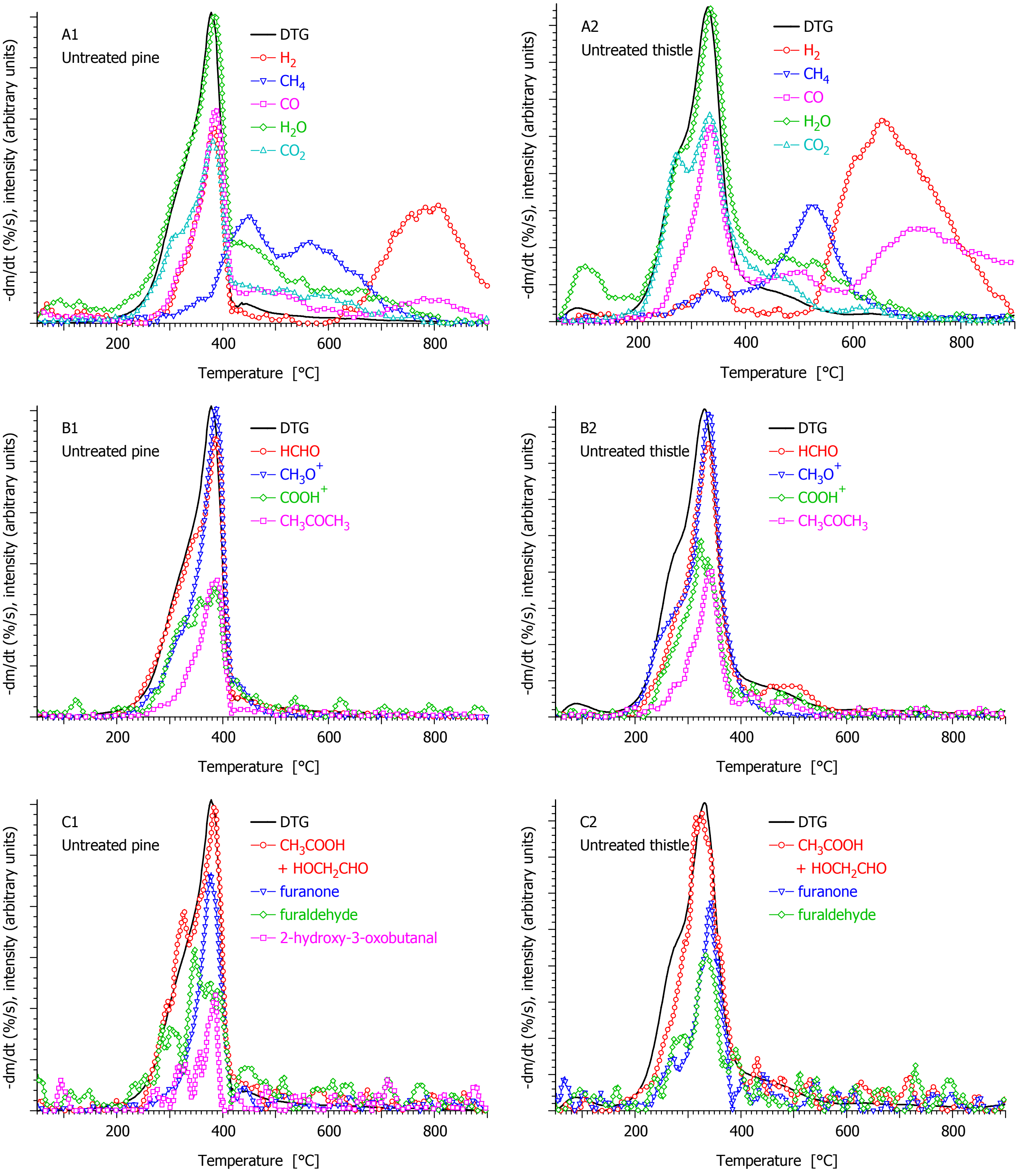

Figure 2. The DTG curves and the evolution profiles of some volatiles released from the pine (panel 1) and the thistle (panel 2) samples.

The formation of a few cyclic products was also detected. Panel C, Figure 2 shows the evolution profiles of some characteristic decomposition products of polysaccharides. The m/z 60 ion can be either acetic acid formed mostly from hemicellulose decomposition or hydroxyacetaldehyde released mainly from cellulose decomposition. The m/z 84 ion corresponds mainly to furanone, the m/z 96 product represents furaldehyde and the m/z 102 ion is mostly 2-hydroxy-3-oxobutanal[4, 5]. As the evolution profiles indicate, furanone and 2-hydroxy-3-oxobutanal are essentially released from cellulose. However, hemicellulose produces more furaldehyde than cellulose. Again, it is important to note that somewhat higher overlap of hemicellulose and cellulose decomposition was observed for the herbaceous crop than for the woody material.

PCA study

Principal component analysis (PCA) has been applied to help the interpretation of the mass spectrometric data. With the help of this method, we are able to distinguish between similar and different objects in our case samples. Namely, the similar objects lie close to one another in the principal components space, while the distance between considerably different samples is large. As a result, the similar objects are arranged into groups. So, PCA is useful for the acquisition of quick information about the similarities in a group of samples[5]. We have considered several groups of variables in the principal components space, so as to the similarities and differences between type of sample, pretreatment, product distribution and range of decomposition can be identified.

The integrated intensities of the most significant ions, H_2O, CO, CO_2 and H2, were considered in the calculations, for selected several temperature ranges of interest: the charring reaction temperature domain for H_2 (between 500 and 900ºC), two step productions for both CO (below and above 600 ºC) and H_2O (adsorptive moisture and the portion produced by decomposition) and the main production zone of CO_2 (between 200 and 750ºC). Different ranges of temperature were considered depending on the sample, since the entire decomposition domain varied between the thistle and the wood. The resulted score plot is shown in Figure 3. The first principal component describes 95% of the total variance and the second is responsible for 5%. From the principal components space, the herbaceous and woody samples are clearly separated, and this separation is more pronounced than the one resulting from the differences between the pretreatments. However, distinction can also be made between them: groups of samples are determined by the water-washing in such a way the extracted and untreated samples are closer than the rest. This fact indicates the very lower effect of the extraction pre-treatment, which only makes a differential effect in thistle.

The loading plot showed in Figure 4 represents the influence of the current variables (the selected MS intensities) on the domain of the two first principal components from PCA. Note that the main differences on the score plot (Figure 3) are observable on the domain of the second principal component, where the main production of CO (below 600 ºC) has the biggest influence (see Figure 4), suggesting a connection between the extraction and the evolution of this product.

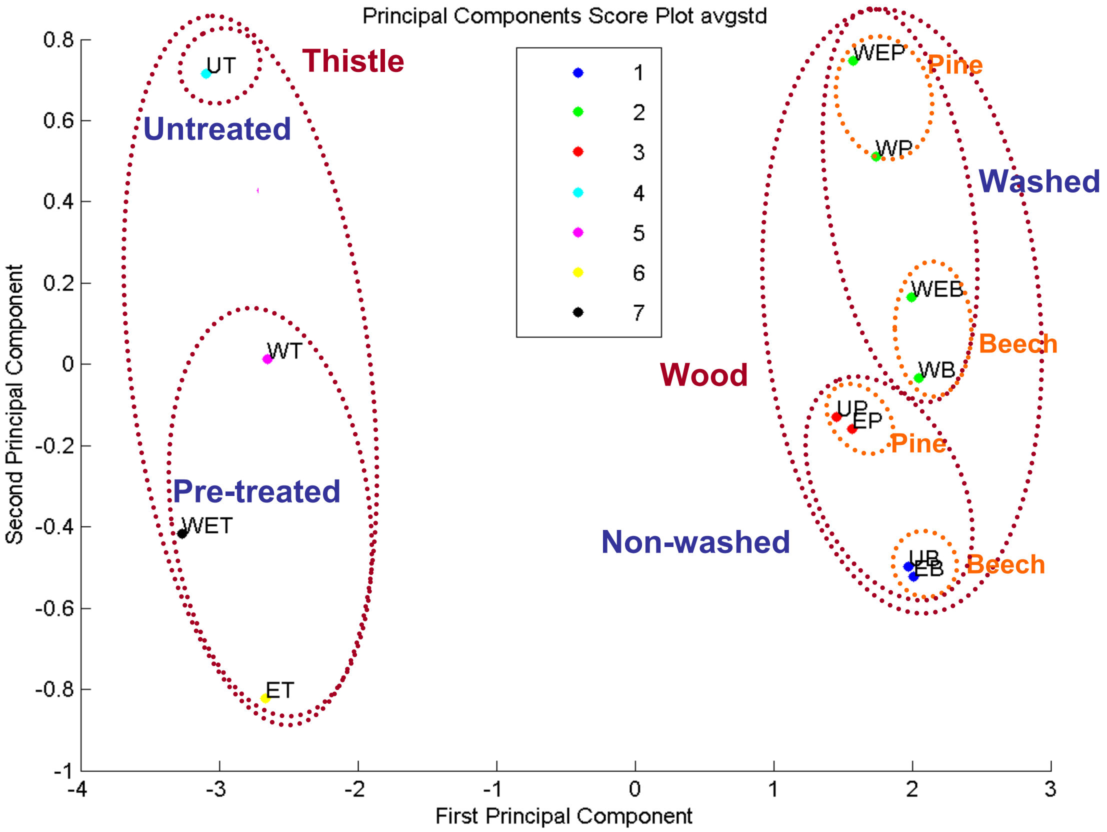

Figure 3. The score plot resulting from the principal components analysis of the main characteristics pyrolysis products: H_2O, CO, CO_2 and H_2.

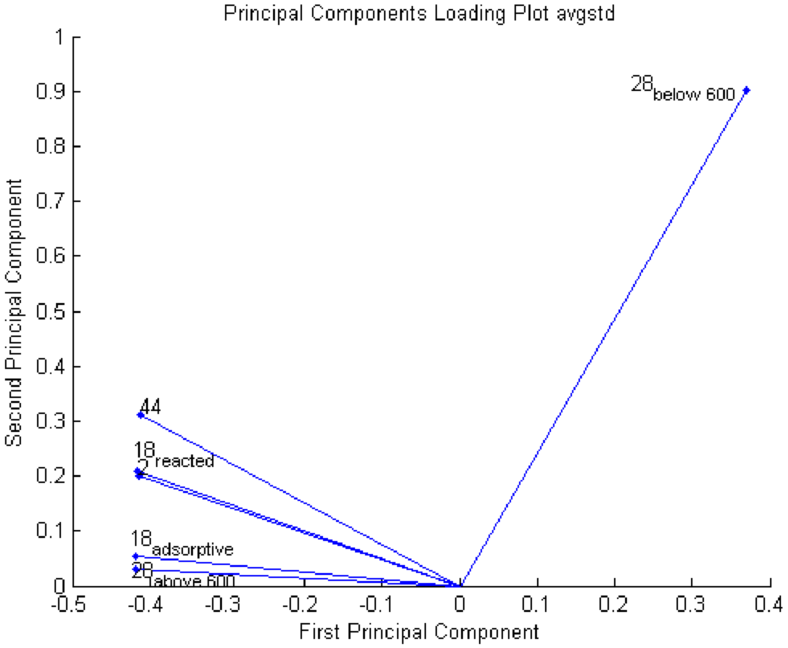

Figure 4. The loading plot from the principal components analysis of the main characteristics pyrolysis products: H_2O, CO, CO_2 and H_2.

Conclusions

The thermogravimetric data and the evolution profiles of low molecular mass products allowed identifying sample specific characteristics for different biomass materials (pine and beech from carpentry residuals and thistle from an energy plantation). The results can be interpreted by the different chemical composition of the wood and thistle. The high lignin content of thistle results in the formation of a high amount of char and methane during thermal decomposition. However, wood decomposition evolves more organic products (aldehydes, acids, ketones, furan derivatives, etc.) due to its higher polysaccharide content. Also, considerable differences have been found with regard to the extractives and inorganic components between the samples. The product distribution is affected by both the organic and inorganic composition of the samples. The two woody samples behave rather similarly. In this case differences in the thermal decomposition can be mainly attributed to the difference in the amount of extractives. The chemometric evaluation (PCA calculations) of the mass spectrometric intensity data of the major products revealed that the difference between the thermal characteristics of wood and thistle is more pronounced than the differences observed from pretreatments.

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