Effect of sample preparation on the thermal degradation of metal-added biomass

Zsuzsa A. Mayer*, Andreas Apfelbacher, Andreas Hornung
European Bioenergy Research Institute (EBRI), *Aston University, Birmingham, B4 7ET, UK*

*Author for correspondence
Tel.: + 44(0)121 204 5298; Fax: + 44(0)121 204 3680. E-mail address:mayerza@aston.ac.uk

Keywords

Analytical pyrolysis; Demineralisation; Dry-mixing; Impregnation; Ion-exchange; Inorganic metal salts

Abstract

The present study investigates the effect of different sample preparation methods on the pyrolysis behaviour of metal-added biomass; Willow samples were compared in the presence of two salts of zinc and lead containing sulphate and nitrate anions which were added to the wood samples with three different techniques as dry-mixing, impregnation and ion-exchange. The effect of acid and water wash as common demineralisation pre-treatments were also analysed to evaluate their roles in the thermal degradation of the biomass. Results from thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and pyrolysis-mass spectrometry (Py-MS) measurements indicated that these pre-treatments change the matrix and the physical-chemical properties of wood. Results suggested that these structural changes increase the thermal stability of cellulose during pyrolysis. Sample preparation was also found to be a crucial factor during pyrolysis; different anions of metal salts changed the weight loss rate curves of wood material, which indicates changes in the primary degradation process of the biomass. Results also showed that dry-mixing, impregnation or ion-exchange influence the thermal behaviour of wood in different ways when a chosen metal salt was and added to the wood material.

1. Introduction

Plant tissues are a mixture of organic compounds and inorganic minerals. Even though these minerals have complex biological functions, they are only regarded as the ash content of the material when biomass is used for energy purposes. The most well-known problems associated with ash during large scale energy conversion technologies are corrosion and metal emission; During large-scale fuel combustion the non-combustible mineral content of the biomass forms deposits in the flue gas channels or boilers and damage the gas turbines to name only a few major problems [1,2]. Besides these corrosive effects metal contaminated biomass combustion can also cause environmental dispersion of toxic trace metals [3,4].

Pyrolysis of biomass with high metal concentration also raises the problems of corrosion and emission [5,6]. The release of metals to the vapour phase degrades the quality and stability of the bio-oil [7]. The right choice of pyrolysis conditions to yield metal free vapours can control the above problems [8,9], and support the accumulation of minerals in the solid bio-char [10,11].

Biomass pyrolysis in the presence of metals is receiving more attention as the number of waste-to-energy projects increase [12-14]. The three main analytical aspects of these investigations are I. Mechanism and kinetics of the biomass degradation, II. Pyrolysis product composition and yield, and III. Metal distribution in the pyrolysis product stream [15-18]. The most common technique of these investigations is thermogravimetric analysis (TGA) [19,20] where the mass loss of the heat-treated samples is recorded and the mass loss rate (differential thermogram, DTG) is calculated. While TGA is a technique to follow thermal decomposition of the solid phase the on-line analysis of pyrolysis products in the gas phase requires coupled analytical methods. These evolved gas analysis (EGA) techniques like TG-IR [18,21], TG-MS [17,22] or Py-MS and Py-GC-MS [23,24] are able to track the formation of the condensable and non-condensable organic compounds while surface ionisation technique can be used to detect the released metal species [2,5]. The investigated samples of these studies are either synthetic biomass (mixture of pure cellulose, hemicellulose and lignin [20,25]), demineralised biomass [6,19,24] or biomass with added metal salts [17,20,21,26]. While samples, prepared with added minerals, can provide information on the effect of selected metals, investigations with the previous two biomass types can prevent measuring the effects of the naturally occurring minerals in the raw biomass. Acid wash is the most common process to remove the inherited mineral matter of the investigated biomass [16,24,25,27] while the general method of metal addition is dry mixing [20,25,26] or impregnation [27-29].

However, these common sample preparation methods raise questions; both impregnation and dry mixing introduce the metal compounds to the biomass as an inorganic salt therefore it is difficult to determine if the observed effects on the degradation of the biomass are related to cations of the added metals, anions of the metal salts or different sample preparation techniques. Therefore, in this study metal ions with two different salt anions were used and three methods for sample preparation were compared.

Due to anthropogenic soil pollution the metal concentration in plants can be several magnitudes higher than the metal levels of plants cultivated in non-contaminated soil. To investigate the effect of metals during pyrolysis, a common energy crop (willow) and two cations, zinc (Zn^{2+}) and lead (Pb^{2+}) were chosen. This deciduous wood is not only a local and representative biomass but also has proved its ability as bioaccumulator in phytoremediation projects [30,31].

Willow stems cultivated in contaminated soil can have as high metal concentrations as 18 ppm of lead or 655 ppm of zinc [18,32] while the relevant metal levels in the raw biomass used in this study were only 1.6 and 51 ppm respectively. The reason why plants from both contaminated and noncontaminated sites show higher zinc levels is that zinc is an essential trace element with good translocation from roots to shoots while lead is a highly toxic metal without biological functions in plants [33,34].

The objective of the study was to observe the effect of a common demineralization process (acid wash) and three different metal cation addition methods with zinc and lead on the pyrolysis behaviour of wood material. To distinguish between the effects of the metal cations and the anions, salt with two different anions were used. Even though chloride salts would have been a self-evident choice, it has been already demonstrated that the presence of chloride and the formation of hydrogen chloride highly effects the biomass decomposition under pyrolysis conditions [17,35], therefore sulphate and nitrate anions were used in this study.

2. Materials and Methods

2.1. Biomass material and characteristics

2.1.1. Wood and metal salts

For the pyrolysis experiments willow (*Salix*) was harvested at St Helens, UK. After removing the leaves the wood material was chipped, pre-dried at 60 °C for 48 h and ground to < 1 mm in a Retsch Knife. For biomass characterisation and demineralisation pre-treatments 0.18-0.85 mm fraction was used (mesh size 80-20) and dried at 105 °C for 24 h. For metal addition and pyrolysis experiments the same fraction of wood particles was grinded further to gain a more homogeneous powder (mesh size 100-80, particles: 0.15-0.18 mm). For sample preparations analytically pure $Zn(NO_3)_2$, $Pb(NO_3)_2$, $ZnSO_4$ and $PbSO_4$ salts were used, purchased from Sigma-Aldrich.

2.1.2. Wood fibre analysis

Besides the ash forming minerals the main components of wood are the extractives and insoluble fibres namely lignin, hemicellulose and cellulose. To estimate the relative amount of each of these lignocellulosic compounds a gravimetry-based wet chemistry method was used [36,37] and the fibre fractions were quantified with a FibreCap 2021 system according to FOSS Application Notes 3804 and 3805.

2.1.3. Proximate and ultimate analysis

The proximate analysis (determination of the volatile matter content and ash content) followed the methods described in the British Standards [38,39] and fixed carbon content was calculated by difference. The elemental composition analysis of the samples (C, H and N) was carried out by an external laboratory and the oxygen content (O) was calculated by difference.

2.1.4. Heating values

To determine the higher and lower heating values of the raw biomass (HHV and LHV) air-dried and grained samples were burned in a Parr 1901 type bomb calorimeter. The basic characteristics of the raw wood are presented in Table 1.

2.2. Biomass demineralisation

To remove the soluble minerals of the wood a common based demineralisation pre-treatment with hydrochloric acid was chosen [40]. After the acid wash, samples were filtered and washed with deionised (DI) water until the effluent was free of chloride. The wood material was dried at 105 °C for 12 h and the ash content, mineral content and other features of the biomass were tested again. Control samples were also prepared with the same demineralisation process, where hydrochloric acid was replaced with deionised water.

2.3. Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

To determine the metal levels of the wood material, samples of 0.25-0.5 g were wet-digested with 5 ml trace analysis grade nitric acid in a microwave reactor. The exact element concentrations of samples were determined by a Perkin Elmer Optima 5300 DV.

2.4. Sample preparation

The three conducted sample preparation methods represent three different interactions between biomass compounds and added metals; while dry mixing does not result any bonding between the lignocellulosic material and the added metals, impregnation is mainly physical adsorption on the surface of the biomass particles. A third technique (ion-exchange) has also been investigated here to simulate the effect of the chemically bounded minerals.

2.4.1. Ion-exchange

2 grams of demineralised wood material was immersed in 40 ml of 0.1 M $Zn(NO_3)_2$ and $Pb(NO_3)_2$ solution, and stirred for approximately 100 h at room temperature. As a next step samples were filtered, washed with deionised water to remove impregnated metals which was followed by the immersion of samples in deionised water for several days during which period the conductivity of the water was checked regularly. When equilibrium had been reached and the conductivity stopped increasing the wood material was filtered and dried at 105 °C for 24 h.

2.4.2. Impregnation and dry mixing

The new metal concentrations of the ion-exchanged samples were determined with ICP-OES and the impregnated and dry mixed samples were prepared to have the same Zn^{2+} and Pb^{2+} concentrations; 2 g of wood material were immersed in 40 ml in each solutions of nitrate and sulphate metal salts. Afterwards the solutions were mixed with a magnetic stirrer until the majority of the water has evaporated then the wood material was dried in the oven at 105 °C for 24 h. For dry mixing the same amount of metal salts were mixed and well-homogenised with 2 g of demineralised wood material.

2.5. Pyrolysis experiments

2.5.1. Thermogravimetric analysis (TGA)

To follow the process of decomposition, raw (untreated), demineralised (pre-treated) and metal added wood samples were pyrolysed in a Mettler TGA/DSC 1 Star System: 10 mg sample in a covered sample pan was heated up from room temperature to 105°C and kept isothermal for 10 minutes to remove the moisture. Consecutively the samples were heated up to 900 °C with a heating rate of 20 °C/min. The flow rate of the He purging gas was kept at 50 cm^3/min during all measurements. All TGA experiments have been repeated several times to ensure the good repeatability of the measurements. For DTG results weight loss rates were calculated and compared.

2.5.2. Evolved gas analysis by Py-MS

To analyse the pyrolysis gases and vapours of the pre-treated, untreated and metal added willow more pyrolysis experiments were conducted with a Py-2020iD Double-Shoot Pyrolyser (Frontier Lab) which was coupled to HP 5972 mass selective detector (MSD) with an Ultra Alloy-5 EGA column (30 m × 0.25 mm, 25 µm) and the system was purged with He carrier gas with a split ratio of 20. During the measurements 0.1-0.5 mg of sample was heated from 50 °C to 800 °C at a rate of 20 °C/min – similar to the conditions of the TGA measurements – while the GC oven temperature was held on a constant 300 °C. Total ion curves of the evolved gases and vapours were recorded with the MSD with an ionization energy of 70 eV and a scanning range from m/z 20-550 with a scanning speed of 1.4 per second.

2.6. FT-IR measurements

To identify structural differences in solid phase 2 mg of ground wood (<62 µm, mesh size 250) was oven dried at 105°C for 12 h blended with 200 mg of potassium bromide, and pressed into pellets. The infrared absorption spectra of the pellets were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer. Four scans per experiments were made in the wavenumber range of 4000-400 cm^{-1} at a resolution of 4 cm^{-1}. Spectra were baseline corrected and normalised to a maximum absorbance of 1.5 for comparison purposes. Band assignation of the spectra was based on the literature [41-48].

3. Results and Discussion

3.1. Metals in raw and demineralised biomass

The demineralisation process successfully removed 99 % of the mineral content of the biomass (the original ash content (1.9 %) decreased to < 0.01 %) and reduced the presence of most of its biomass minerals (Ca: 5410/86 ppm; K: 1962/37 ppm; Mg: 330/10 ppm; Na: 188/44 ppm; Zn: 51/15 ppm before and after the pre-treatment, respectively) except Si, which had the same level (28/28 ppm) before and after the acid wash pre-treatment.

3.2. Effects of pre-treatments on the thermal decomposition of the biomass

Thermal decomposition depends on both the organic and inorganic structure of the biomass and the measured mass loss rate curves from TGA measurements (derivative thermogravimetric curves, DTG) can be interpreted as the independent degradation of the three main organic woody biomass compounds, cellulose, hemicellulose and lignin [49,50]. In case of the untreated willow sample (**a,** in Fig. 1.) the characteristic thermal decomposition temperatures of hemicellulose (at 200-350 °C), cellulose (at 320-400 °C) and broad peak of lignin with small intensity (at 250-550 °C) can be clearly identified [41].

The untreated and demineralised samples have their initial degradation temperatures at around 200 °C and their cellulose decomposition gave the most intense DTG peaks. While these peaks have similar intensity (i.e. degradation rate) the thermal decomposition temperature of acid-washed sample shifted from 373 °C to 376 °C. Water treatments also shifted the degradation temperatures of cellulose peaks when the demineralisation pre-treatment was conducted with DI water or when acid washed wood was soaked in DI water and gave peak temperatures at 383 °C and 381 °C respectively (not shown). These shifts to higher temperature indicate that the pre-treated cellulose has a higher thermal stability which also explains the reported higher activation energy of the pre-treated wood materials [27].

Similar shifts were reported during the pyrolysis of wood and straw demineralised with water or acid. The broadly accepted explanation for this phenomenon is the absence of the inorganic promoted cellulose decomposition [17,19,20].

The overlapping peaks of the mass loss rate temperature of the solid phase (DTG curves) and the peak temperature of the mass spectrometric total ions curves (TIC) of the forming gases (**c,** in Fig. 1.) show that the TGA and Py-MS methods can be regarded as complementary analytical techniques. The main observed difference in case of the demineralised sample is the presence of the signal at 650 °C which was identified as levoglucosan (m/z: 60, 57, 73, 43, 56, 70, 45), a main decomposition product of cellulose [51,52].

Comparing the total ion curves (**b,** in Fig. 1.) for the untreated and demineralised samples it can be seen that significantly more levoglucosan was forming during the pyrolysis of the wood in the presence of the original minerals of the biomass. The EGA peak of levoglucosan appears at higher temperature than expected which indicates that levoglucosan can retain in the interface due to its polarity [51].

Another clearly observable difference between the DTG curves of untreated and demineralised wood material (**a,** in Fig. 1.) is the absence of the shoulder around 300 °C, related to the degradation of hemicellulose. Fibre analysis results indicate that the aggressive acid wash pre-treatment reduced the hemicellulose content of the sample from 19.4 % to 3.5 % (Fig. 2.) therefore it is highly probable that the absence of the peak is not an effect of the reduced mineral content of the sample. The fibre analysis results of the raw and pre-treated samples also indicate that the relative content of cellulose remained the same approximately

(40.9 % and 42.3 % respectively) while lignin content ostensibly increased from 32.7 % to 51.3 %. As lignin resist acid hydrolysis more than the other biomass compounds therefore this lignin content was used as a reference value to normalise the results of the fibre analysis. The normalised results show that the absolute cellulose content decreases by 35 % which indicates that the acid wash significantly reduced not only the hemicellulose but the cellulose content as well.

To obtain more information on the structural changes in wood FT-IR measurements were conducted with samples with and without demineralisation pre-treatments. The FT-IR spectra of untreated willow (**a**), acid washed willow (**b**), water washed willow (**c**) and acid washed than water soaked willow (**d**) are shown in Figure 3.

In the mid-infrared spectra the first strong broad band between 3700 and 3000 cm^{-1} is the sum of overlapping stretching vibrations of O–H functional groups. In the region of 2975-2840 cm^{-1} the unresolved group of medium weak bands is related to C-H stretching vibrations of CH_2 and CH_3 groups. The peak around 1730 cm^{-1} assigned to the absorption of free carbonyl groups, therefore it is a typical hemicellulose marker [41,43,44,48]. The next two bands around 1600 and 1500 cm^{-1} are generaly considered as lignin markers [43,44,47,53] as this is the region of the skeletal vibrations of aromatic rings.

In the fingerprint region of wood (1500 to 400 cm^{-1}), the spectra contain at least six bands in the C-O streching region between 1200-950 cm^{-1} that are most probabely cellulose-related absorptions [45]. Both acid and water-based treatments seem to sharpen these bands which might indicate changes in interaction between the C-OH, C-O-C and other functional groups.

One of the most significant changes in the spectra of acid washed samples is the decrease of the hemicellulose peak at 1730 cm^{-1} (**b,** and **d,** in Fig. 3.) which is in agreement with the results of the fiber analysis. The band around 1600 cm^{-1} is normally assigned as a lignin marker [43,44,53]; however, it is difficult to exclude the presence of other C=C vibrations or the deformation vibration of water adsorbed in KBr pellets [54].

Pretreatments also effects the O-H vibrations of wood; the original ratio of the two strong and non-separated bands at 3424 and 3343 cm^{-1} as revealed by curve fitting was 1 to 0.9. Acid wash decreased band intensity at 3424 cm^{-1} and increased the intensity of the band at 3343 cm^{-1} with a ratio of 1:0.92. The intensity ratio of the same band components in water-washed wood (**c**) and acid-washed wood soaked in water (**d**) is changed to 1:0.98 and 1:1, respectively, indicating water related changes in wood structure. As hydrogen-bonded OH groups have lower streching frequencies than free alcohols [42] and stronger H-bonds result in band shifts to lower frequencies [55], we assume that the formation of new or stronger H-bonds led to these changes in the FT-IR spectra. The band at 3343 cm^{-1} with increasing intensity may also be assigned as O-H vibration with interchain H-bonds between the cellulose fibers [45]. The presence of new interchain bonds could explain the increased thermal stability of the demineralised samples during TGA measurements, however, band assignation of FT-IR spectra contains uncertainties due to the presence of water.

There is another observation which does not support the hypothesis of the shifted cellulose degradation temperatures caused by biomass minerals; pre-treatment and pyrolysis experiments were repeated with ashless cellulose (Whatman filter paper, Grade 44 purchased from Sigma-Aldrich) and the peak degradation temperautre of acid-washed and water-soaked paper was also found to be shifted by 8-10 °C to the higher temperature region compared to untreated cellulose (TGA curves not shown).

Even though it seems that the lack of biomass minerals cannot be blamed for the increased thermal stability of cellulose in demineralised wood the hypothesis of new H-bond formation should be tested by other analytical methods. Furthermore, the effect of metals on the thermal degradation of biomass is unquestionable and it is the subject of our ongoing research.

3.3. Effect of anions on the decomposition of metal added biomass

The most typically used metal addition method is impregnation when biomass material is soaked in the salt solution then the solvent is gradually evaporated [28,29,56]. In this study samples were impregnated with different metal salts containing two different anions to compare their thermal behaviour during pyrolysis experiments. The detected difference between the measured DTG curves of the lead nitrate and lead sulphate impregnated samples is the presence of a shoulder around 270 °C (**a,** in Fig. 4). The source of this weight loss might be the degradation of the biomass catalysed by the decomposing salt of the chemically non-bounded $Pb(NO_3)_2$ salt.

Comparing the weight loss rate curves of zinc sulphate and zinc nitrate impregnated willow (**b,** Fig. 4.) no metal salt degradation can be observed. The zinc sulphate lowered the peak temperature of the impregnated willow ($T_{Zn\text{-}nitrate}$: 374 °C; $T_{Zn\text{-}sulphate}$: 359 °C) and the shape of the DTG curves are markedly different. These changes during the solid phase decomposition indicate that the present of the zinc sulphate significantly affects the primary degradation mechanism of the wood material. It is also observed that samples prepared with sulphate salt had lower degradation rate compare to samples prepared with nitrate salts.

3.4. Cation exchange in wood

After soaking the acid-washed wood material in the solutions of metal nitrates the samples were washed several times with deionised water until the conductivity of the rinse water matched that of the original deionised water indicating that unbound metals and salts from the surface of the particles have been completely removed. As the next step, samples were soaked in deionised water and the conductivity was checked regularly and found to be increased for several days, indicating that the wood behaved as an ion-exchanger and added metal ions were bound reversibily to acidic groups [53]. This ion-exchange feature of the cell wall components in wood is also known to be preventing the translocation of toxic metals from roots to shoots [30,57].

The zinc and lead concentrations in the ion-exchanged and dried biomass samples were found to be 3543 and 18730 ppm respectively which indicates that the metal binding capacity of cell walls in the wood material is stronger for lead than for zinc.

3.5. Effect of the different metal addition methods

Figure 5 shows the thermal decomposition of the acid-washed willow samples which was dry-mixed, impregnated or ion-exchanged with lead nitrate. (To have more comparable results the DTG curves have been normalised as the ion-exchanged sample gave slightly higher weight loss rate.) Even though the three samples contained lead ion in the same concentration (18730 ppm) their individual sample preparation methods led to characteristically different peak temperatures (dry-mixed: 373 °C; impregnated: 378°C; ion-exchanged: 381°C). The DTG curves of both the impregnated and the dry-mixed samples have peaks around 270 °C which might be related to the decomposition of $Pb(NO_3)_2$ salt. The degradation curve of the ion-exchanged sample lack this peak as nitrate anions and unbound salt have been washed off during the sample preparations.

During the sample preparation wood was soaked in water solutions of metal salts, except the dry-mixed samples. For the very same reason control measurements were performed with demineralised wood with and without a water-soaking step. The peak temperature of the demineralised control wood material was 376 °C (result not shown) which is 3°C higher than the peak temperature of the wood sample dry-mixed with lead-nitrate (——Fig. 5.; T_{peak}: 373°C). The other control sample was demineralised then soaked in clean deionised water over a period of 4 days and gave a peak temperature of 381 °C (result not shown), while the peak temperature of the impregnated sample was 378 °C (– - –Fig. 5.) therefore the observed shift after the metal addition was -3 °C again. The zinc exchanged sample (···· Fig. 5.; T_{peak}: 381 °C) gave the same peak temperature as the above mentioned control. Zinc cation in the absence of nitrate anion did not appear to have any catalytic or inhibitor effect on the thermal behaviour of wood.

4. Conclusion

A common energy wood (Salix) was characterised, acid washed and metal added in two different metal salt forms (sulphate and nitrate) for analytical scale pyrolysis experiments. Prior to the demineralisation step the fuelwood characteristics of the wood material were determined and both metal content and fiber content were measured before and after the acid wash pre-treatment. Chemical structure changes in wood material were also investigated with FT-IR As a next step demineralised samples were metal salt added by means of dry-mixing, impregnation and ion-exchange with the same metal ion concentrations. To follow the decomposition of the raw, demineralised and metal added samples and a well defined pyrolysis heating rate (20 °C/min) was chosen and results obtained from TGA and Py-MS measurements were compared.

Demineralisation pre-treatments have a strong influence on the FT-IR spectra of wood due to its structural changes. Demineralisation with HCl can effectively decrease the mineral content of wood but it also changes its primary polymer structure, decreases the hemicellulose content.

Gravimetric analysis was used to compare the pyrolysis behaviour of samples impregnated with sulphate and nitrate salts of the same metal. Wood prepared with zinc sulphate and zinc nitrate gave markedly different degradation patterns indicating that the anion of the metal salts can have significant impact on the degradation of impregnated wood. Samples impregnated with lead sulphate and lead nitrate gave less different degradation patterns, however, an extra peak with small intensity was detected. Impregnation is mainly physical adsorption on the particle surface, therefore it is assumed that this weight loss was related to the release of discrete nitrate salt. Similar peak was also observed on the DTG curve of sample dry-mixed with lead nitrate. This peak was expected as dry addition does not lead to the formation of chemical bounds between inorganic salts and the organic phase of wood. A third sample preparation approach (ion-exchange) was also analysed for differences. Eventhough this appears to be the only method to investigate the thermal decomposition of biomass with chemically bounded metal cations and without the presence of salt anions, very few examples can be found in literature [16,58]. Measurements presented in this study were strongly influenced by the pre-treatments of wood, the metal addition methods and the presence of the metal salt anions. As a general conclusion wood material pyrolysed in the presence or absence of metals and minerals must be prepared carefully to gain reliable and comparable results.

Acknowledgements

Financial support has been provided by the Science Bridge Project (EP/G039992/1), the initiative of the Research Councils (RCUK) and Department of Science and Technology (DST).

The authors wish to thank Richard Collins and Anne Nuttall (Coventry University) for their guidance with ICP-OES measurements, David Bielawski, Bob Massingham and Brian Johnson (Environmental Protection Department, St Helens) for support of this work and Josephine Mmojieje and Po Chu for the assistance in the lab. Z.A.M. is also grateful to Dr. Gábor Keresztury (CRC-HAS, Budapest), Dr. Philip Davies and Dr. James Titiloye (Aston University) for their valuable comments.

References

[1] L.L. Baxter, T.R. Miles, B.M. Jenkins, T. Milne, D. Dayton, R.W. Bryers and L.L. Oden, The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences, Fuel Process. Technol. 54, (1998) 47.

[2] K.O. Davidsson, B.J. Stojkova and J.B.C. Pettersson, Alkali emission from birchwood particles during rapid pyrolysis, Energy & Fuels. 16, (2002) 1033.

[3] C. Boman, M. Öhman and A. Nordin, Trace element enrichment and behavior in wood pellet production and combustion processes, Energy & Fuels. 20, (2006) 993.

[4] W.P. Linak and J.O.L. Wendt, Toxic metal emissions from incineration: Mechanisms and control, Prog. Energy Combust. Sci. 19, (1993) 145.

[5] J.G. Olsson, U. Jaglid, J.B.C. Pettersson and P. Hald, Alkali metal emission during pyrolysis of biomass, Energy & Fuels. 11, (1997) 779.

[6] D.M. Keown, G. Favas, J.I. Hayashi and C.Z. Li, Volatilisation of alkali and alkaline earth metallic species during the pyrolysis of biomass: differences between sugar cane bagasse and cane trash, Bioresour. Technol. 96, (2005) 1570.

[7] R. Fahmi, A.V. Bridgwater, I. Donnison, N. Yates and J.M. Jones, The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability, Fuel. 87, (2008) 1230.

[8] H.W. Wu, D.M. Quyn and C.Z. Li, Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part III. The importance of the interactions between volatiles and char at high temperature, Fuel. 81, (2002) 1033.

[9] N. Sonoyama, T. Okuno, O. Masek, S. Hosokai, C.Z. Li and J. Hayashi, Interparticle desorption and re-adsorption of alkali and alkaline earth metallic species within a bed of pyrolyzing char from pulverized woody biomass, Energy & Fuels. 20, (2006) 1294.

[10] L. Koppolu, R. Prasad and L. Davis Clements, Pyrolysis as a technique for separating heavy metals from hyperaccumulators. Part III: pilot-scale pyrolysis of synthetic hyperaccumulator biomass, Biomass Bioenergy. 26, (2004) 463.

[11] C. Lievens, J. Yperman, T. Cornelissen and R. Carleer, Study of the potential valorisation of heavy metal contaminated biomass via phytoremediation by fast pyrolysis: Part II: Characterisation of the liquid and gaseous fraction as a function of the temperature, Fuel. 87, (2008) 1906.

[12] A. Porteous, Energy from waste incineration - A state of the art emissions review with an emphasis on public acceptability, Appl. Energy. 70, (2001) 157.

[13] T. Malkow, Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal, Waste Manage. 24, (2004) 53.

[14] A. Hornung and A. Apfelbacher, ”Biomass processing”, US Patent 12/992,647, Nov 15, 2010

[15] P.T. Williams and P.A. Horne, The role of metal salts in the pyrolysis of biomass, Renewable Energy. 4, (1994) 1.

[16] M. Kleen and G. Gellerstedt, Influence of inorganic species on the formation of polysaccharide and lignin degradation products in the analytical pyrolysis of pulps, J. Anal. Appl. Pyrolysis. 35, (1995) 15.

[17] M. Müller-Hagedorn, H. Bockhorn, L. Krebs and U. Müller, A comparative kinetic study on the pyrolysis of three different wood species, J. Anal. Appl. Pyrolysis. 68-69, (2003) 231.

[18] C. Lievens, R. Carleer, T. Cornelissen and J. Yperman, Fast pyrolysis of heavy metal contaminated willow: Influence of the plant part, Fuel. 88, (2009) 1417.

[19] C. Di Blasi, C. Branca and G. D'Errico, Degradation characteristics of straw and washed straw, Thermochim. Acta. 364, (2000) 133.

[20] H. Yang, R. Yan, H. Chen, C. Zheng, D.H. Lee and D.T. Liang, Influence of mineral matter on pyrolysis of palm oil wastes, Combust. Flame. 146, (2006) 605.

[21] A. Jensen, K. Dam-Johansen, M.A. Wójtowicz and M.A. Serio, TG-FTIR Study of the Influence of Potassium Chloride on Wheat Straw Pyrolysis, Energy & Fuels. 12, (1998) 929.

[22] G. Várhegyi, M.J. Antal, E. Jakab and P. Szabó, Kinetic modeling of biomass pyrolysis, J. Anal. Appl. Pyrolysis. 42, (1997) 73.

[23] R. Alén, E. Kuoppala and P. Oesch, Formation of the main degradation compound groups from wood and its components during pyrolysis, J. Anal. Appl. Pyrolysis. 36, (1996) 137.

[24] I.-Y. Eom, K.-H. Kim, J.-Y. Kim, S.-M. Lee, H.-M. Yeo, I.-G. Choi and J.-W. Choi, Characterization of primary thermal degradation features of lignocellulosic biomass after removal of inorganic metals by diverse solvents, Bioresour. Technol. 102, (2011) 3437.

[25] K. Raveendran, A. Ganesh and K.C. Khilar, Influence of mineral matter on biomass pyrolysis characteristics, Fuel, 74, (1995) 1812.

[26] H. Yang, R. Yan, H. Chen, C. Zheng, D.H. Lee and D.T. Liang, In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin, Energy & Fuels. 20, (2006) 388.

[27] D.J. Nowakowski, J.M. Jones, R.M.D. Brydson and A.B. Ross, Potassium catalysis in the pyrolysis behaviour of short rotation willow coppice, Fuel. 86, (2007) 2389.

[28] A. Khelfa, G. Finqueneisel, M. Auber and J.V. Weber, Influence of some minerals on the cellulose thermal degradation mechanisms - Thermogravimetic and pyrolysis-mass spectrometry studies, J. Therm. Anal. Calorim. 92, (2008) 795.

[29] L. Koppolu, F.A. Agblevor and L.D. Clements, Pyrolysis as a technique for separating heavy metals from hyperaccumulators. Part II: Lab-scale pyrolysis of synthetic hyperaccumulator biomass, Biomass Bioenergy. 25, (2003) 651.

[30] I.D. Pulford and C. Watson, Phytoremediation of heavy metal-contaminated land by trees - A review, Environ. Int. 29, (2003) 529.

[31] M. Mleczek, Z. Kaczmarek, Z. Magdziak and P.K. Golinski, Hydroponic estimation of heavy metal accumulation by different genotypes of Salix, J. Environ. Sci. Health. Part A Toxic/Hazard. Subst. Environ. Eng. 45, (2010) 569.

[32] E. Meers, B. Vandecasteele, A. Ruttens, J. Vangronsveld and F. Tack, Potential of five willow species (Salix spp.) for phytoextraction of heavy metals, Environ. Exp. Bot. 60, (2007) 57.

[33] J.W. Huang, J. Chen, W.R. Berti and S.D. Cunningham, Phytoremediation of lead-contaminated soils: role of synthetic chelates in lead phytoextraction, Environ. Sci. Technol.31, (1997) 800.

[34] G. Hacisalihoglu and L.V. Kochian, How do some plants tolerate low levels of soil zinc? Mechanisms of zinc efficiency in crop plants, New Phytol. 159, (2003) 341.

[35] F. Shafizadeh, R.H. Furneaux, T.G. Cochran, J.P. Scholl and Y. Sakai, Production of levoglucosan and glucose from pyrolysis of cellulosic materials, J. Appl. Polym. Sci. 23, (1979) 3525.

[36] H.K. Goering and P.J. Van Soest, Forage Fiber Analysis (Apparatus, Reagents, Procedures and Some Application), Research Service, U.S. Department of Agriculture (ARS USDA), Washington DC, 1970.

[37] D.R. Mertens, Gravimetric determination of amylase-treated neutral detergent fiber in feeds with refluxing in beakers or crucibles: collaborative study, J. AOAC Int. 85, (2002) 1217.

[38] British Standards Institute, 2009. BS EN 15148: Solid biofuels — Determination of the content of volatile matter. London: British Standards Institute

[39] British Standards Institute, 2009. BS EN 14775: Solid biofuels — Determination of ash content. London: British Standards Institute

[40] D.J. Nowakowski and J.M. Jones, Uncatalysed and potassium-catalysed pyrolysis of the cell-wall constituents of biomass and their model compounds, J. Anal. Appl. Pyrolysis. 83, (2008) 12.

[41] H. Yang, R. Yan, H. Chen, D.H. Lee and C. Zheng, Characteristics of hemicellulose, cellulose and lignin pyrolysis, Fuel, 86, (2007) 1781.

[42] G. Socrates, Infrared characteristic group frequencies, Wiley New York, 1980.

[43] N. Owen and D. Thomas, Infrared Studies of "Hard" and "Soft" Woods, Appl. Spectrosc. 43, (1989) 451.

[44] K.K. Pandey, A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy, J. Appl. Polym. Sci. 71, (1999) 1969.

[45] Y. Maréchal and H. Chanzy, The hydrogen bond network in Ib cellulose as observed by infrared spectroscopy, J. Mol. Struct. 523, (2000) 183.

[46] C.G. Boeriu, D. Bravo, R.J.A. Gosselink and J.E.G. van Dam, Characterisation of structure-dependent functional properties of lignin with infrared spectroscopy, Ind. Crops Prod. 20, (2004) 205.

[47] M. Schwanninger, J.C. Rodrigues, H. Pereira and B. Hinterstoisser, Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose, Vib. Spectrosc. 36, (2004) 23.

[48] R. Bodîrlău and C. Teacă, Fourier Transform Infrared Spectroscopy and Thermal Analysis of Lignocellulose Fillers Treated with Organic Anhydrides, Rom. Journ. Phys., 54, (2007) 93.

[49] M.J. Antal, Jr. and G. Várhegyi, Cellulose Pyrolysis Kinetics: The Current State of Knowledge, Ind. Eng. Chem. Res. 34, (1995) 703.

[50] G. Skodras, P. Natas, P. Basinas and G.P. Sakellaropoulos, Effects of pyrolysis temperature, residence time on the reactivity of clean coals produced from poor quality coals, Global NEST Journal, 8, (2006) 89.

[51] D. Fabbri, G. Chiavari, S. Prati, I. Vassura and M. Vangelista, Gas chromatography/mass spectrometric characterisation of pyrolysis/silylation products of glucose and cellulose, Rapid Commun. Mass Spectrom. 16, (2002) 2349.

[52] S. Helle, N.M. Bennett, K. Lau, J.H. Matsui and S.J.B. Duff, A kinetic model for production of glucose by hydrolysis of levoglucosan and cellobiosan from pyrolysis oil, Carbohydr. Res. 342, (2007) 2365.

[53] I. Gaballah and G. Kilbertus, Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks, J. Geochem. Explor. 62, (1998) 241.

[54] V.M. Malhotra, S. Jasty and R. Mu, FT-IR Spectra of Water in Microporous KBr Pellets and Water's Desorption Kinetics, Appl. Spectrosc., 43, (1989) 638.

[55] G.C. Pimentel and A.L. McClellan, The hydrogen bond, W. H. Freeman And Company, San Francisco and London, 1960.

[56] P. Szabó, G. Várhegyi, F. Till and O. Faix, Thermogravimetric/mass spectrometric characterization of two energy crops, Arundo donax and Miscanthus sinensis, J. Anal. Appl. Pyrolysis. 36, (1996) 179.

[57] M. Ghosh and S. Singh, A review on phytoremediation of heavy metals and utilization of it's by products, Applied Ecology and Environmental Res. 3, (2005) 1.

[58] G.N. Richards and G. Zheng, Influence of metal ions and of salts on products from pyrolysis of wood: Applications to thermochemical processing of newsprint and biomass, J. Anal. Appl. Pyrolysis. 21, (1991) 133.

Figures

Fig. 1.

Thermal degradation of willow. **a,** DTG curves of untreated and demineralised willow from TGA measurements; **b,** Total Ion Curves of the evolved gases from PY-MS measurements; **c,** Comparison of the solid phase degradation and evolved gas formation of demineralised willow

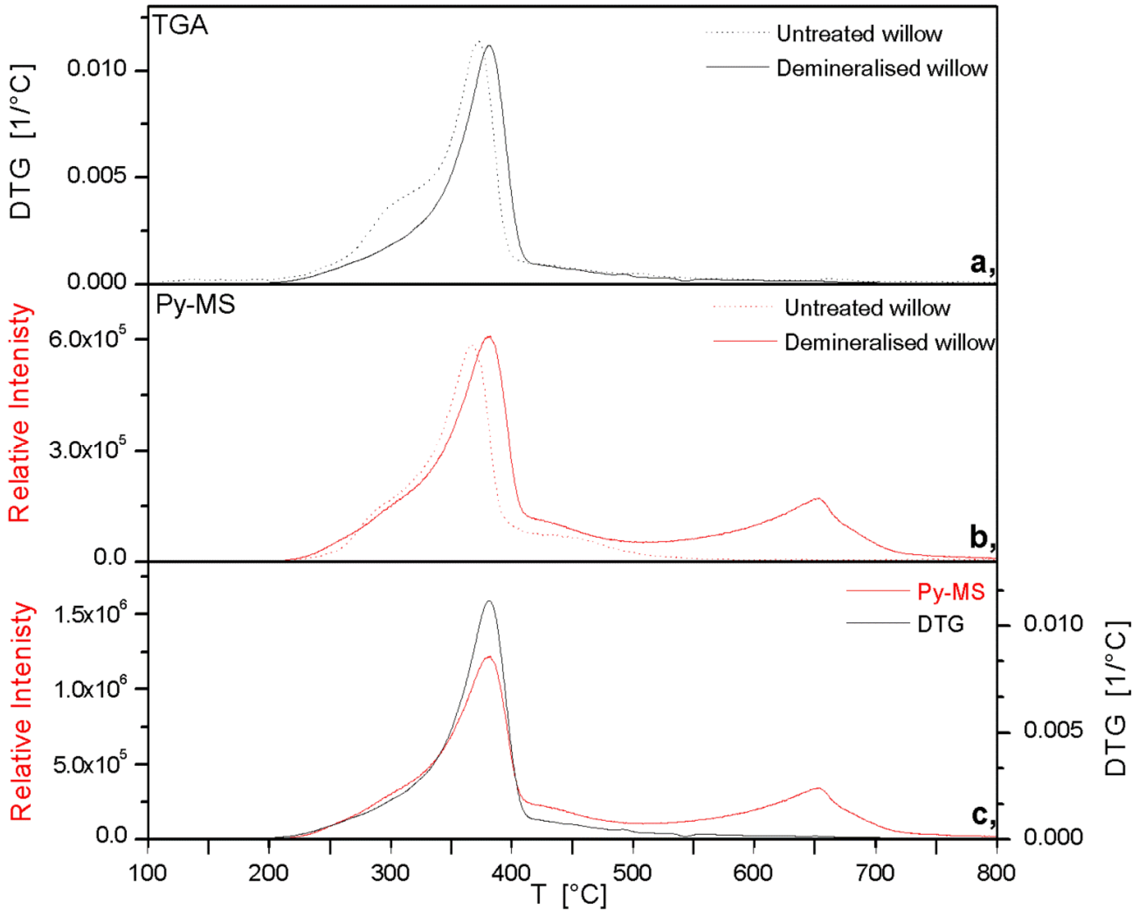

Fig. 2.
Ash and fibre content of the raw and acid washed biomass

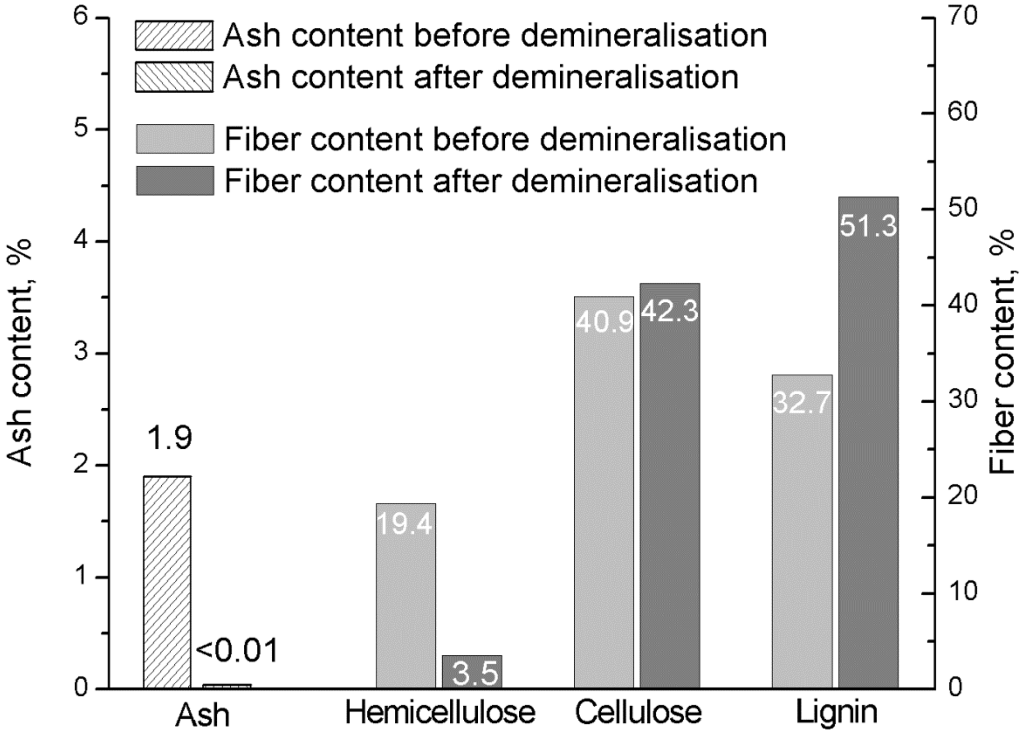

Fig. 3.
FT-IR spectra of raw willow (**a**), acid washed willow (**b**), water washed willow (**c**) and acid washed willow soaked in water (**d**)

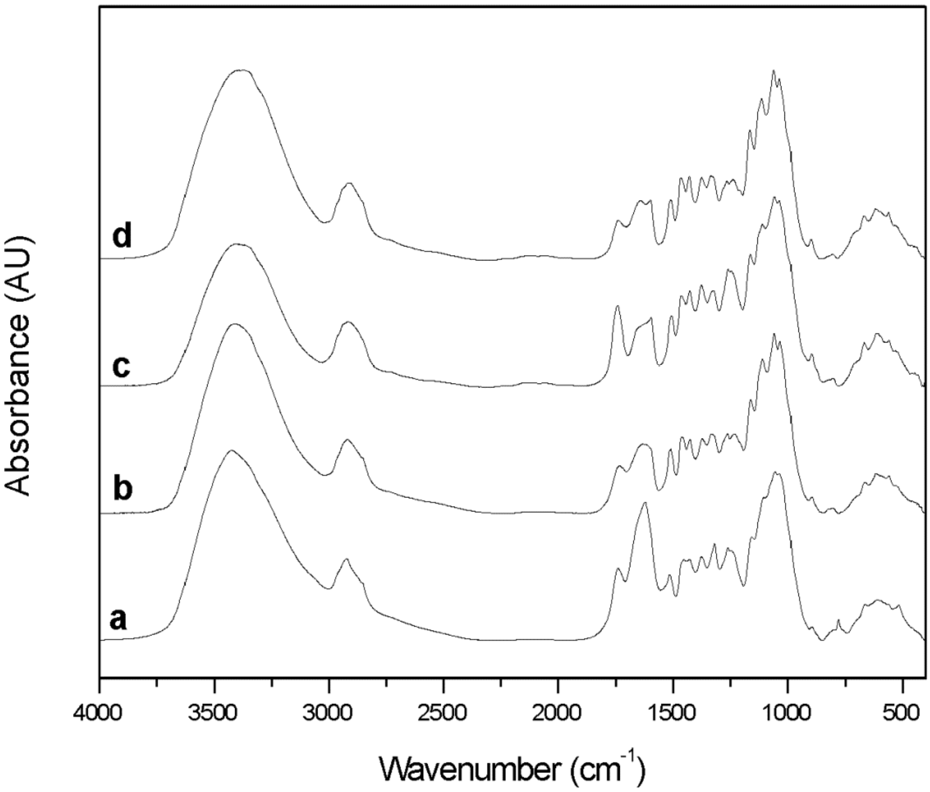

Fig. 4.
Demineralised willow impregnated with lead nitrate and lead sulphate salts (**a**); and demineralised willow impregnated with zinc nitrate and zinc sulphate salts (**b**)

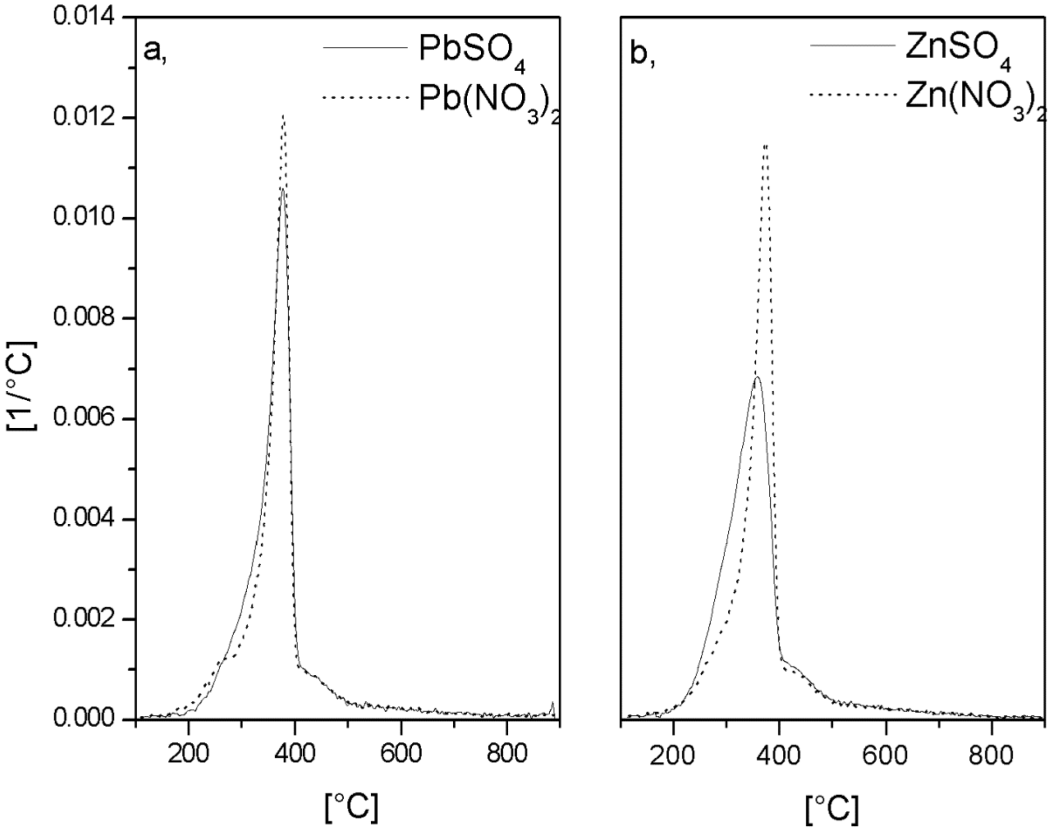

Fig. 5.
Weight loss rate curves of acid washed willow samples prepared with lead ion

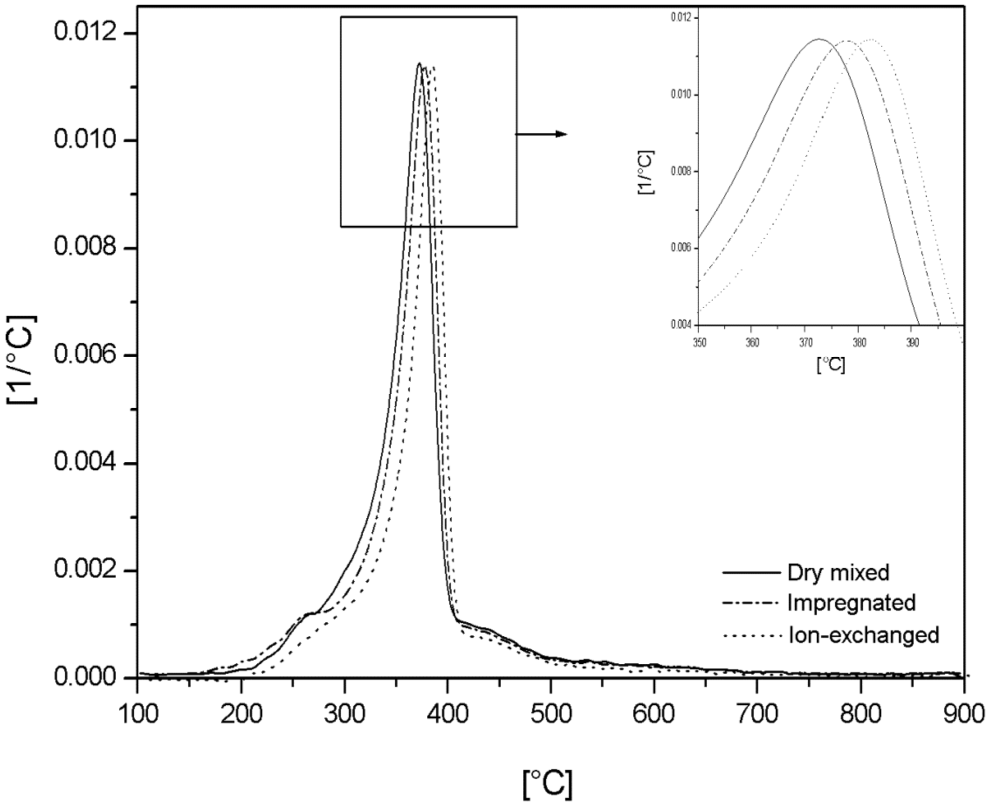

Table 1

Basic characteristics of the untreated willow

Relative composition, % (dry and ash free basis)		**Ultimate Analysis, % (dry basis)**		**Proximate Analysis, % (dry basis)**		**Energy Content (MJ/kg)**	
Extractives	7.0	C	48.75	Fixed Carbon	16.7	HHV	19.7
Hemicelluloses	19.4	H	6.05	Volatiles	81.4	LHV	18.3
Cellulose	40.9	N	0.47	Ash	1.9		
Lignin	32.7	O	44.73				