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A comparative study on the pyrolysis of metal- and ash-enriched wood and the combustion properties of the gained char

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Abstract

This study aims to investigate the pyrolysis behaviour of metal-contaminated wood and the combustion properties of char derived from wood pyrolysis. Seven metals (Na, Mg, Ca, Zn, Cd, Pb and Fe(III)) were introduced to willow in cation form by ion-exchange and the thermal behaviour of demineralised samples and samples with additional ash were also investigated.

The results show that the char yield increased from 21 % to 24–28 % and levoglucosan yield in vapour phase decreased from 88 % to 62-29 % after the addition of inorganic compounds, even though the metal binding capacity of wood varied from one metal ion to another. While char yield seems to be effected mainly by the concentration of the metal ions, levoglucosan yield was more dependent on the ionic species especially when sodium ions were present. When combustion experiments were carried out with char made of the metal enriched wood, two consecutive steps were observed, both effected by the presence of inorganic compounds. The first step was identified as the release and combustion of volatiles, while the second peak of the burning profile is the actual combustion of the fixed carbon. The burnout temperatures, estimated ignition indices and the conversion indicate that the type and not the amount of metal ions were the determining factors during the second step of combustion.

1. Introduction

While the fossil fuel crisis urges the utilisation and extension of biomass and other renewable energy sources, the application of biomass raises new problems like the efficiency of the energy conversion technology or the availability of lands for fuel crop cultivation. Ideally bioenergy production should not compromise food crop security. Alternative biomass

sources should be used more widely, like agricultural waste, refuse-derived materials and contaminated biomass.

As the number of waste-to-energy projects increases [1,2], the pyrolysis of metal contaminated biomass is also receiving more attention. Two examples for the increased metal content in pyrolysis feedstock is metal uptake by plants during the remediation of contaminated soil and the decontamination of metal containing effluents with plant parts [3-5]. The most common analytical technique to investigate the pyrolytic behaviour of metal contaminated biomass is thermogravimetric analysis [4,6-8]. Despite of the similarities in the applied analytical methods, there are several contradictions in the literature concerning the effect of metals, especially on biomass degradation temperature [6,8,9] or on product yield [6,10-13].

Biomass char (BC) is the solid co-product of the pyrolysis process and it is a renewable energy source with a heating value up to 30-35 MJ/kg [14]. Due to its oxygen content and incoherent carbon structure BC has higher reactivity than coal [15,16] and higher energy density and better combustibility properties than traditional biomass [17]. Changes in the physicochemical properties of char during combustion has been investigated with a relatively wide variety of analytical tools [16,18,19], however, very little is known about the effects of metals during BC combustion [20,21].

Similar to char, bio-oil is also a valuable product of biomass pyrolysis but not only for energy applications. Levoglucosan (1,6-anhydro-β-D-glucopyranose), and other compounds found in bio-oil, have the additional potential to act as renewable resource for chemicals. Levoglucosan (LG) is the primary decomposition product of cellulose, therefore a main compound in wood derived bio-oils [22,23]. Biomass pyrolysis offers the possibility for industrial scale LG production [10,24] for chemical synthesis and fermentation processes [25,26], however, LG yield is highly sensitive to the conditions of pyrolysis [25] or to the presence of metals [27].

The main aim of this study was to qualify and quantify the influence of different metal cations on wood pyrolysis and char combustion. Our previous study evidenced that different sample preparation methods (e.g. impregnation or dry-mixing) and the presence of metal salt anions can lead to changes in the thermal behaviour of wood and metal-addition by ion-exchange can eliminate these problems [28]. In this study demineralised wood was ion-exchanged with sodium (Na^{+}), magnesium (Mg^{2+}), calcium (Ca^{2+}), zinc (Zn^{2+}), cadmium (Cd^{2+}), lead (Pb^{2+}) and iron (Fe^{3+}) ions or enriched with ash and pyrolysed in a

thermogravimeter. A set of combustion experiments were also conducted with pyrolysis-derived char to estimate the effect of inorganic compounds during these energy conversion processes. Another objective of this study was to compare levoglucosan yields during the pyrolysis of metal-exchanged wood.

2. Experimental

2.1. Materials

2.1.1. Biomass characterisation

The wood used in pyrolysis experiments was willow harvested at St Helens, UK. After removing the leaves the wood 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 ground to finer and more homogeneous powder (mesh size 100-80). The basic characteristics of the raw willow are presented in Table 1. The in-depth description of wood preparation and fuelwood characterisation can be found in a recent study [28].

2.1.2. Demineralised Biomass

To reduce the original ash content of the biomass the soluble mineral matter of wood was washed out with 2.0 M hydrochloric acid (HCl) [29].

2.1.3. Ash

Untreated wood was subjected to air oxidation in a muffle furnace according to BS EN 14775 British standard [30] and the remaining ash was collected for further experiments.

2.1.4. Ion-exchanged wood, cellulose and lignin

Ion-exchanged samples were prepared with the following method: 2 g of demineralised wood material was immersed in 40 ml of 0.1 M metal-nitrate solution, and stirred for approximately 100 h at room temperature. Control sample was soaked in DI water and prepared the same way. As a next step samples were filtered, washed with DI water to remove impregnated metals and nitrate anions. This procedure was followed by the immersion of samples in deionised water for several days while 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 12 h. For sample preparations analytically pure nitrate salts were used (from Sigma-Aldrich). To compare the

ion-exchange behaviour of the pure biomass compounds the same metal addition process was conducted with organosolv lignin (from Repap Technologies Inc.) and with microcrystalline cellulose powder (from Sigma-Aldrich).

2.1.5. Biomass char

To determine the burning profile of BC, samples were produced the following way: prior to char production wood samples (raw willow, demineralised willow, willow with added ash and ion-exchanged willow) were fractionated on a 60-mesh screen and char samples were produced at 500 °C in a muffle furnace under N_2 atmosphere.

2.2. Methods

2.2.1. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

To determine the mineral content of willow, approximately 0.5 g of samples 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. Inorganic compounds in demineralised and metal added samples were analysed by the same method.

2.2.2. Analytical Pyrolysis and Thermogravimetric Analysis (TGA)

To follow the process of decomposition of raw, demineralised and metal or ash added wood, samples were pyrolysed in a Mettler TGA/DSC 1 Star System; 10 mg sample was heated up from room temperature to 105 °C and kept isothermal for 10 minutes to remove moisture. Consecutively the samples were heated up to 900 °C with a heating rate of 20 °C/min. The flow rate of the helium purging gas was kept at 50 cm^3/min during all measurements. All recorded weight loss was converted to derivative weight loss marked as rate of weight loss in figures.

2.2.3. Pyrolysis GC-MS measurements

Pyrolysis of wood was also performed in a Py-GC-MS system a Py-2020iD Double-Shoot Pyrolyser (Frontier Lab) which was coupled to HP 5972 mass selective detector (MS) with a DB-1701 column (60 m × 0.25 mm, 25 μm) and the system was purged with He carrier gas with a split ratio of 20. To analyse the gas phase of pyrolysis 0.1-0.2 mg wood was dropped to the 550 °C furnace and vapour products were separated on the column while the GC oven was heated from 40 °C to 290 °C at a rate of 3 °C/min. Separated compounds were recorded with the MS detector with an ionization energy of 70 eV and a scanning range of m/z 20-550 and scanning speed of 1.4 per second.

Pyrolysis products were identified by comparing key fragment ions with NIST 98 Mass Spectral Library and literature data [31]. Product yields were estimated by comparing the measured peak areas.

2.2.4. Non-isothermal char combustion

5.0 mg biomass char was combusted in a Mettler TGA/DSC 1 Star System under a constant airflow of 50 cm^3/min while the temperature increased from 25 to 900 °C with 20 °C/min heating rate. Both weight loss curves and heat flow were recorded and combustion properties of char were estimated by characterisation methods developed for coal and coal-char blends [32-35].

To monitor the gas emission of the combustion experiments a Pfeiffer QuadStar-200 mass spectrometer was coupled to the thermogravimetric analyser with an in-house constructed and externally heated coupling system. Key fragment ions were scanned in the range of m/z 2-80 with ionisation energy of 70 eV and 0.24/sec scanning speed.

2.2.5. Data analysis

TGA measurements and pyrolysis experiments of well homogenised samples gave good and repeatable results with small variation in T_{max} values (±2 °C) and in char yields (±1 %). Char combustion experiments were more sensitive to sample size than wood pyrolysis, therefore careful attention was paid to use the same amount of sample (5.0 mg) during each measurement. Weight loss curves from char combustion had ±2 °C variation in both T_{max} and *BOT* values and ±0.003 1/min in R_{max} values. The average values of the repeated measurements are collected in Table 2 and 3.

Collected data were also used for general regression analysis; F-test was used to check the relationship between charge and metal bounding capacity then to scrutinise the effect of charges and metal ion concentrations on pyrolysis product yields with Statistica 7.0 software program. As the experiments have not been designed for statistical analysis therefore results are only for general observations.

3. Results and Discussion

3.1. Ion-exchanged wood, lignin and cellulose

Prior to demineralisation process the major constituents of inorganic compounds, identified in willow in a previous study, were calcium, potassium magnesium, sodium, zinc and silica with a total ash content of 1.9 wt % [28]. To distinguish between the effects of the

inherited and the added metals the raw biomass was washed with HCl. This demineralisation pre-treatment removed 99 % of the inherited biomass metals (ash content < 0.01 %), however, when HCl was replaced with DI water the measured ash content remained high (1.3 wt %). Differences between water and acid-based pre-treatments indicate that some of the biomass minerals in willow are in water soluble inorganic salt form while others can resist water treatment. These metals can be bound to the organic matrix of wood by associating with oxygen-containing functional groups of the biomass polymers like carboxyl groups in cellulose or phenolic groups in lignin [3,36].

To compare the ion-bonding properties of wood, acid pre-treated willow was saturated in the high concentration solution with $NaNO_3$, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Zn(NO_3)_2$, $Cd(NO_3)_2$, $Pb(NO_3)_2$ and $Fe(NO_3)_3$ salts then washed and filtered to remove nitrate anions. The measured concentration of heavy metals in wood were found to be the followings: Pb: 18730; Cd: 5374; Fe: 4823; and Zn: 3543 ppm (Fig.1). The concentrations of alkali and alkaline earth metals of Ca, Mg and Na were only 1820, 683 and 378 ppm, respectively, which indicates that these metals bund reversibly and can be more easily removed during water wash.

After repeating the same ion-exchange procedure with pure cellulose, the trend was found similar to wood; lead concentration was the highest (808 ppm) followed by Cd (456 ppm), Fe (193 ppm) and Zn (194 ppm) while concentration of Ca, Na and Mg were 157, 127 and 110 ppm, respectively. Compare to wood and cellulose, lignin shows a different behaviour; when it was ion-exchanged with Cd cation it resulted lower metal concentration than lignin loaded with Mg or Ca cations (58, 86 and 145 ppm, respectively) and more lead, iron and zinc ions were bound in lignin (3555, 683, 241 ppm) less sodium (39 ppm), compared to pure cellulose.

Both cellulose and lignin had significantly lower metal content after the ion-exchange step than demineralised wood. This indicates that pre-treatment enhanced the metal bounding capacity of wood by activating the acidic groups [3]. Even though it was suggested that lignocellulosic materials have higher efficiency to divalent metal ions than to monovalent ions [7], regression analysis results indicate that the charge of the metal ions had no significant effect on the measured metal concentration in wood, cellulose or lignin (p = 0.7; 0.6 and 0.83, respectively). However, there were several parameters which were excluded in this study like pH of the solvents, the radii of the metal ions etc.

3.2. Effect of ash and added metals on the pyrolytic behaviour of wood

3.2.1. Thermal stability of untreated, pre-treated and metal added wood

Weight loss curves of willow pyrolysis ((—) on Fig.2a) shows the characteristic thermal decomposition temperatures of hemicellulose (200-350 °C), cellulose (320-400 °C) and a broad peak with smaller intensity (250-550 °C) which is related to lignin degradation [37]. The peak temperatures of cellulose degradation shifted to higher region when the inorganic compounds of the wood were washed out ((—) demineralised willow, Fig.2b) and to lower temperature regions when approximately 2 wt % ash has been added to untreated or demineralised wood ((····) on Fig.2a and b). Added ash did not seem to change the degradation pattern of hemicellulose or lignin extensively. Another clearly observable difference between the degradation curves of untreated and demineralised wood material is the absence of the hemicellulose related shoulder around 300 °C. Fibre analysis results indicated that the acid wash reduced the hemicellulose content of the sample from 19.4 % to 3.5 % [28], therefore the absence of the shoulder was presumably not an effect of the reduced mineral content of the sample.

Ion-exchanged wood was also pyrolysed to investigate the effect of the individual metal ions without the presence of the inherited biomass minerals. Similarities in the shapes of the weight loss curves indicate that metals of ion-exchanged wood did not change the main degradation pathways in solid phase, however, some of the added metal ions led to a shift in peak temperatures of cellulose degradation (Fig. 3); iron and zinc seem to catalyse the cellulose degradation, while calcium and lead inhibited it by shifting the peak temperature to higher temperature ranges.

3.2.2. Biomass char yield

Char yield was slightly sensitive to the presence of added ash; both the pyrolysis of untreated willow and willow with added ash yielded approximately 28 % BC. The absence of ash dropped the BC yield to 21 % and increased back to 27 % when ash was “replaced” to demineralised wood ((—) and (····) on Fig. 2b). There was an extra weight loss peak detected around 700 °C during the pyrolysis of the ash added willow which was followed by CO_2 formation which suggests that ash catalysed the carbon conversion to CO_2 in char.

The pyrolysis of ion-exchanged wood was followed by enhanced BC formation (Table 2), except in case of sodium where there was a minor decrease from 21 to 20 %. Other metals increase BC yield up to 28 %. Moreover increases in BC yield show similar trend to the

initial metal concentrations and statistical results indicate that the measured char yields are not independent from metal concentrations in wood (p=0.04). It was previously suggested that divalent metals can enhance char yield by forming crosslinks [38], however, no significant regression was found between BC yield and the charge of the metal ions (p=0.1).

3.2.3. Levoglucosan yield

Inorganic compounds affect not only the char and gas formation but also the distribution of compounds forming bio-oil. The most significant difference between the representative chromatograms of willow pyrolysis (Fig. 4) is that demineralisation pre-treatment increased the peak are of LG from 10 to 88 %. LG formation has been described as acid-catalysed degradation of cellulose [10,22] therefore this increase can be explained with the nature of the demineralisation pre-treatment which was performed with HCl.

The highest LG yield was found in vapour phase (over 90%) when pure cellulose was pyrolysed. The cellulose-to-levoglucosan conversion decreased when metal ions were added to biomass and the cellulose-to-LG conversion ranged between 29 % (Na) and 62 % (Mg). When results were tested by regression analysis it was found that metal concentration has no significant effect on LG yield (p =0.6), so it is a selective catalytic or inhibitor effect of the metal ions; LG formation could be depressed in its primary forming reaction in the presence of inorganic compounds [39]. Furthermore some metals – especially sodium – are known cracking catalyst of biomass vapours in secondary reactions [40] which can also result smaller LG yield [41,42] in agreement with the results presented in Table 2.

3.3. Combustion properties of the biomass char

Biomass pyrolysis is the volatilization and thermal degradation of the organic compounds and biopolymers in inert atmosphere which lead to the accumulation of the inorganic compounds in char [43,44]. The effect of inherited and added metals on the burning properties of BC was investigated via a series of combustion experiments. BC from demineralised, ash-added and ion-exchanged wood was also prepared and the burning profiles of char samples were compared.

The results of the non-isothermal combustion experiments indicate that thermal behaviour of BC in oxidative atmosphere is similar to coal [32-34]; two successive mass loss rate peaks were observed during BC combustion of willow and demineralised willow (Fig. 5a) within the temperature range of the 270 °C (*initial combustion temperature*) and 637 °C

(*burnout temperature*, *BOT*) with a total conversion (C_{total}) of 88-97 %. The main characteristics of char combustion are presented in Table 3.

Evolved gas analysis shows that the formation of the detected ions (m/z: 18, H_2O^+ and 44, CO_2^+) followed the patterns of the weight loss curve at lower temperature region with a maximum around 325 °C (Fig. 7). C_xH_y fragment ions (e.g. $C_3H_3^+$ and $C_3H_7^+$) were also detected with smaller abundance. TGA measurements with char heated under inert atmosphere also release volatiles between 300 and 400 °C (curves not shown) which indicate that BC samples contain organic compounds beside of the pyrogenic carbon. Therefore, the first step of BC combustion was identified as the release of these hydrocarbons. Although char samples were prepared on 500 °C where the thermal degradation of the main wood compounds is finished, heat transfer problems during BC preparation could lead to incomplete carbonisation. Other possible explanation for the presence of these volatiles is that the longer residence time of gases – compare to pyrolysis in a constantly purged TGA system – favoured to the repolimerisation of vapours which remained in char [45].

The maximum rate of this weight loss reaction was between 315-325 °C and was followed by the combustion of the released vapours indicated by the CO_2 and water formation and the detected exothermic peak shown on Fig. 5b. The shift in the maxima of the weight loss rate and heat flow peak temperatures can be explained with delays in oxygen diffusion [46].

The heat flux curves of char combustion have also two regions (Fig. 5b). Both regions were exothermic with maximum heat flow rates of 16 and 26 Wg^{-1} with slightly varying peak temperatures than the weight loss rate curves.

The first rapid weight loss step of BC combustion was followed by a slower reaction. This second reaction is the actual combustion of the carbon rich char, evidenced by exothermic heat flow and CO_2 formation. Similar to the pyrolysis experiments, the combustion of samples with high ash content have an additional peak around 700 °C (Fig. 5a), however, as this temperature is over *BOT*, therefore this change in the solid phase is not related to the carbon content of the char. The ash in char has other effects on the combustion of BC. While demineralisation delayed the burnout of the char, the ash-added shifted *BOT* to lower temperatures. As the relative ratio of inorganic compounds is increasing during the combustion process it was expected to find more differences around *BOT* in the presence of ash-added. Comparison of the shapes of the weight loss rate curves in this region demonstrates that solid phase reactions were different and inherited ash catalysed char

combustion by a different mechanism than added ash (see also angular and horizontal arrows on Fig. 5a).

Fig. 5a. demonstrates another significant difference: ash enhances the volatile release of char significantly at the lower temperature range (300-350 °C) of BC combustion. It is also known that both the primary formation and secondary reactions of volatiles are sensitive to the presence of inorganic compounds [47,48] and heterogeneously catalysed oxidation of volatiles can explain this increase in weight loss in the presence of ash [49]. DeGroot et al. [50] also reported the catalytic and inhibiting properties of inorganic additives which effected the oxidation properties of char but not the structure therefore it can be concluded that the observed changes are related to the oxidation of the volatiles or char but not to the structural changes of the BC.

Fig. 6 shows the burnout profiles of BC prepared from ion-exchanged wood. The weight loss rate curves do not seem to follow one pattern which implies the different roles of each metal cations on the combustion of BC. However, similarly to the heat flow results of Fig. 5b, two maxima were observed in the heat release profile (Fig. 6b) and show some other similarities to the combustion behaviour of the ash added samples. The similar R_{max} values from the second step of BC combustion indicates that the absence or presence of biomass minerals and inorganic compounds do not increased or decreased char reactivity significantly but the total conversion of the ash and metal added BC was found to be lower. When the original ash content was removed then replaced by added ash, the C_{total} remained the same (92 %) but the *BOT* decreased. To estimate the actual effect of ash on the ignition performance of BC, ignition indices (D_i) were also determined [35,51]. The char derived from demineralised willow gave the smallest D_i ($8.33 \cdot 10^{-5}$). D_i had a maximum when the original ash content of willow was doubled prior to char formation ($9.27 \cdot 10^{-5}$). Ion-exchange also decreased C_{total} and slightly increased R_{max}, and metals shifted *BOT* to lower temperature regions by 11-83 °C. The ignition indices of these char samples increased to 9.17- 9.58 $\cdot 10^{-5}$ compared to the original $8.33 \cdot 10^{-5}$ D_i value of the control char. These results clearly indicate that ash and added metals promote char decomposition and combustion. Based on the assumption that most inorganic compounds accumulate in char [43,44] statistical calculations suggested that the shifts in *BOT* and the estimated values of C_{total} and D_i were not related to the initial metal concentrations of willow (p = 0.20, 0.16 and 0.22, respectively).

4. Conclusion

The results of analytical scale experiments dealing with the influence of demineralisation and added ash on the thermal degradation of wood in inert atmosphere and biochar during combustion have been described. Metal added willow was prepared with 7 different cations by ion-exchange. The main advantage of this sample preparation technique is that the thermal behaviour of the samples loaded with individual metal ions can be investigated in the absence of metal salt anions.

The thermal stability of samples was compared by recording their weight loss curves during pyrolysis. Differential scanning calorimetry and thermogravimetry were also used to study the combustion behaviour of char residue of the pyrolysed wood materials. The applied analytical techniques were used successfully to determine changes in fuel properties of wood and biomass and results indicate that:

(1) Cellulose, the main cell wall component of wood, can bind more metals than lignin.

(2) The metal binding capacity of wood and its cell wall components are stronger in case of heavy metals like lead and cadmium than for alkali earth and alkaline metals.

(3) The presence of Ca, Fe, Pb and Zn ions slightly changed the main degradation peak temperature of cellulose while Na, Mg and Cd ions did not seem to affect the mass loss rate during pyrolysis.

(4) Demineralisation decreased, while added inorganic compounds increased the char yield during pyrolysis.

(5) Char formation was influenced mainly by the quantity and not the quality of the added metal ions.

(6) The relative concentration of levoglucosan in vapour phase was decreased when wood was pyrolysed in the presence of added metals or ash.

(7) The results of the regression analysis indicate that levoglucosan yield of wood pyrolysis was mainly affected by the type and not the total amount of the added inorganics.

(8) Weight loss curves of the analytical scale pyrolysis evidenced that the carbonization of willow was completed around 500 °C. However, bench scale pyrolysis at 500 °C resulted char with high volatile content and char combustion led to the release of these volatiles.

(9) The consecutive steps of BC combustion were identified, namely the release and combustion of vapours and the combustion of fixed carbon.

(10) Inorganic compounds in BC affected the first step of combustion differently but slightly increased combustion reactivity (rate of weight loss) during the second step of combustion.

(11) Both ash and added metals acted as promoters during char combustion by decreasing the burnout temperature and increased the ignition performance of char.

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References

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

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

[3] 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.

[4] 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.

[5] M. Stals, R. Carleer, G. Reggers, S. Schreurs and J. Yperman, Flash pyrolysis of heavy metal contaminated hardwoods from phytoremediation: Characterization of biomass, pyrolysis oil and char/ash fraction, J. Anal. Appl. Pyrol., 89, (2010) 22.

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

[7] 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. Pyrol., 35, (1995) 15.

[8] 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. Pyrol., 68-69, (2003) 231.

[9] 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.

[10] 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.
[11] K. Raveendran, A. Ganesh and K.C. Khilar, Influence of mineral matter on biomass pyrolysis characteristics, Fuel, 74, (1995) 1812.
[12] 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.
[13] 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.
[14] C. Ryu, V.N. Sharifi and J. Swithenbank, Waste pyrolysis and generation of storable char, Int. J. Energy Res., 31, (2007) 177.
[15] R.I. Backreedy, J.M. Jones, M. Pourkashanian and A. Williams, Burn-out of pulverised coal and biomass chars, Fuel, 82, (2003) 2097.
[16] E. Henrich, S. Bürkle, Z.I. Meza-Renken and S. Rumpel, Combustion and gasification kinetics of pyrolysis chars from waste and biomass, J. Anal. Appl. Pyrol., 49, (1999) 221.
[17] M. Saghir, Co-combustion of biomass and biochar, M.Sc. Thesis, 2009, Aston University, Birmingham, UK
[18] M.J. Wornat, R.H. Hurt, N.Y.C. Yang and T.J. Headley, Structural and compositional transformations of biomass chars during combustion, Combust. Flame, 100, (1995) 131.
[19] A.M.C. Janse, H.G. de Jonge, W. Prins and W.P.M. van Swaaij, Combustion kinetics of char obtained by flash pyrolysis of pine wood, Ind. Eng. Chem. Res., 37, (1998) 3909.
[20] J. Jones, A. Williams, L. Darvell, M. Nawaz and X. Baxter, The role of metals in biomass pyrolysis, char formation and char properties, at: Science in Thermal and Chemical Biomass Conversion, Victoria, Canada, Sept 2004.
[21] J. Jones, L. Darvell, M. Pourkashanian and A. Williams, The role of metals in biomass char combustion, Proceedings of the European Combustion Meeting (Louvain-la-Neuve), 8, (2005) 9.
[22] C.M. Lakshmanan and H.E. Hoelscher, Production of levoglucosan by pyrolysis of carbohydrates. Pyrolysis in hot inert gas stream, Ind. Eng. Chem. Prod. Res. Develop, 9, (1970) 57.
[23] P.R. Patwardhan, J.A. Satrio, R.C. Brown and B.H. Shanks, Product distribution from fast pyrolysis of glucose-based carbohydrates, J. Anal. Appl. Pyrol., 86, (2009) 323.
[24] D. S. Scott, J. Piskorz and D. Radlein, Production of levoglucosan as an industrial chemical, in: E.J. Witczak (Ed.), Levoglucosenone and levoglucosans: Chemistry and applications, ATL Press, Washington, 1994, pp. 179-188.
[25] X.L. Zhuang, H.X. Zhang, J.Z. Yang and H.Y. Qi, Preparation of levoglucosan by pyrolysis of cellulose and its citric acid fermentation, Bioresour. Technol, 79, (2001) 63.
[26] 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.
[27] 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. Pyrol., 21, (1991) 133.

[28] Z.A. Mayer, A. Apfelbacher and A. Hornung, Effect of sample preparation on the thermal degradation of metal-added biomass, J. Anal. Appl. Pyrol., 94. (2012) 170.
[29] 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. Pyrol., 83, (2008) 12.
[30] British Standards Institute, 2009. BS EN 14775: Solid biofuels — Determination of ash content. London: British Standards Institute
[31] O. Faix, I. Fortmann, J. Bremer and D. Meier, Thermal degradation products of wood; Gas chromatographic separation and mass spectrometric characterization of polysaccharide derived products, Eur. J. Wood Wood Prod., 49, (1991) 213.
[32] J.W. Cumming and J. McLaughlin, The thermogravimetric behaviour of coal, Thermochim. Acta, 57, (1982) 253.
[33] S.E. Smith, R.C. Neavel, E.J. Hippo and R.N. Miller, DTGA combustion of coals in the Exxon coal library, Fuel, 60, (1981) 458.
[34] M. Serageldin and W.P. Pan, Coal analysis using thermogravimetry, Thermochim. Acta, 76, (1984) 145.
[35] S.G. Sahu, P. Sarkar, N. Chakraborty and A.K. Adak, Thermogravimetric assessment of combustion characteristics of blends of a coal with different biomass chars, Fuel Process. Technol., 91, (2010) 369.
[36] C. Bayley and G.R.F. Rose, Metal-organic complexes formed during the treatment of wood with metal salts, Nature, 185, (1960) 313.
[37] H. Yang, R. Yan, H. Chen, D.H. Lee and C. Zheng, Characteristics of hemicellulose, cellulose and lignin pyrolysis, Fuel, 86, (2007) 1781.
[38] M.J. Wornat and P.F. Nelson, Effects of ion-exchanged calcium on brown coal tar composition as determined by Fourier transform infrared spectroscopy, Energy Fuels, 6, (1992) 136.
[39] 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.
[40] M. Nik-Azar, M.R. Hajaligol, M. Sohrabi and B. Dabir, Mineral matter effects in rapid pyrolysis of beech wood, Fuel Process. Technol., 51, (1997) 7.
[41] A. Pattiya, J.O. Titiloye and A.V. Bridgwater, Fast pyrolysis of cassava rhizome in the presence of catalysts, J. Anal. Appl. Pyrol., 81, (2008) 72.
[42] P.R. Patwardhan, J.A. Satrio, R.C. Brown and B.H. Shanks, Influence of inorganic salts on the primary pyrolysis products of cellulose, Bioresour. Technol., 101, (2010) 4646.
[43] L. Koppolu, R. Prasad and L. D. 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.
[44] 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. Characterization of the liquid and gaseous fraction as a function of the temperature, Fuel, 87, (2008) 1906.
[45] P.C. Lewellen, W.A. Peters and J.B. Howard, Cellulose pyrolysis kinetics and char formation mechanism, Symposium (International) on Combustion, 16, (1977) 1471.
[46] M Otero, , L.F Calvo, , A Morán, Analysis of the co-combustion of sewage sludge and coal by TG-MS, Biomass Bioenergy, 22, (2002) 319.

[47] C.A. Zaror, I.S. Hutchings, D.L. Pyle, H.N. Stiles and R. Kandiyoti, Secondary char formation in the catalytic pyrolysis of biomass, Fuel, 64, (1985) 990.
[48] M.J. Antal, Jr. and G. Várhegyi, Cellulose Pyrolysis Kinetics: The current state of knowledge, Ind. Eng. Chem. Res., 34, (1995) 703.
[49] G. Löffler, V.J. Wargadalam and F. Winter, Catalytic effect of biomass ash on CO, CH_4 and HCN oxidation under fluidised bed combustor conditions, Fuel, 81, (2002) 711.
[50] W.F. DeGroot and F. Shafizadeh, Influence of inorganic additives on oxygen chemisorption on cellulosic chars, Carbon, 21, (1983) 61.
[51] X. Li, B. Ma, L. Xu, Z. Hu and X. Wang, Thermogravimetric analysis of the co-combustion of the blends with high ash coal and waste tyres, Thermochim. Acta, 441, (2006) 79.

Captions

Fig. 1.
Mass distribution of inorganic elements in ion-exchanged wood, cellulose and lignin

Fig. 2.
Weight loss curves of wood pyrolysis from TGA measurements

Fig. 3.
Weight loss curves of ion-exchanged wood pyrolysis from TGA measurements

Fig. 4.
Pyrograms of untreated, pre-treated and ash added wood samples from Py-GC-MS measurements

Fig. 5.
Burning profile of char from TGA-DSC measurements.
Weight loss rate during combustion (**a**), Heat released during combustion (**b**)

Fig. 6.
Burning profile of char in the presence of added metals.
Weight loss rate during combustion (**a**), Heat released during combustion (**b**)

Char of willow previously ion-exchanged with **1**, Na^{+}; **2**, Mg^{2+}; **3**, Ca^{2+}; **4**, Zn^{2+}; **5**, Fe^{3+}; **6**, Cd^{2+}; **7**, Pb^{2+}.

Fig. 7.
Ion current curves from combustion TG-MS studies of char prepared form demineralised willow in the presence of external ash

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 [a]				

[a] By difference

Table 2

Table 2. Measured char and levoglucosan yields of wood pyrolysis obtained from TGA and Py-GC-MS measurements

Wood sample	**Char yield** (wt %)	**LG yield** (% in vapour phase)
Control	21	88
+ Na	20	29
+ Mg	24	62
+ Ca	25	55
+ Zn	24	56
+ Fe(III)	25	61
+ Cd	25	46
+ Pb	28	41

Table 3. Combustion characteristics of the biomass char

	T_{max} [a] (°C)	R_{max} [b] (1/min)	*BOT* (°C)	C_{total} (wt %)	D_i [c] (x 10^{-5})
Willow	485	0.072	597	92	8.63
+ ash	472	0.075	552	88	9.27
Demineralised willow	526	0.074	637	97	8.33
+ ash	473	0.071	584	92	8.45
Ion-exchanged willow					
Control	526	0.074	637	97	8.33
+ Na	561	0.082	626	94	9.27
+ Mg	528	0.082	602	95	9.39
+ Ca	494	0.081	587	91	9.58
+ Zn	534	0.085	600	92	9.45
+ Fe(III)	500	0.075	569	91	9.50
+ Cd	520	0.076	561	95	9.17
+ Pb	446	0.075	554	89	9.25

[a] T_{max}: Peak temperature where rate of weight loss of carbon combustion was maximum

[b] R_{max}: Maximum rate of weight loss corresponds to actual char combustion.
$R_{max} = - dw/dT_{max} \cdot 1/w_0$, where w_0 is the initial weight of the char

[c] D_i: Ignition index. $D_i = R_{max} /(t_{max} \cdot t_{in})$ where t_{in} is the start of the initial ignition time of sample (approximately 24 min at 270 °C) and t_{max} is the time when the combustion rate was at its maximum (33-37 min).

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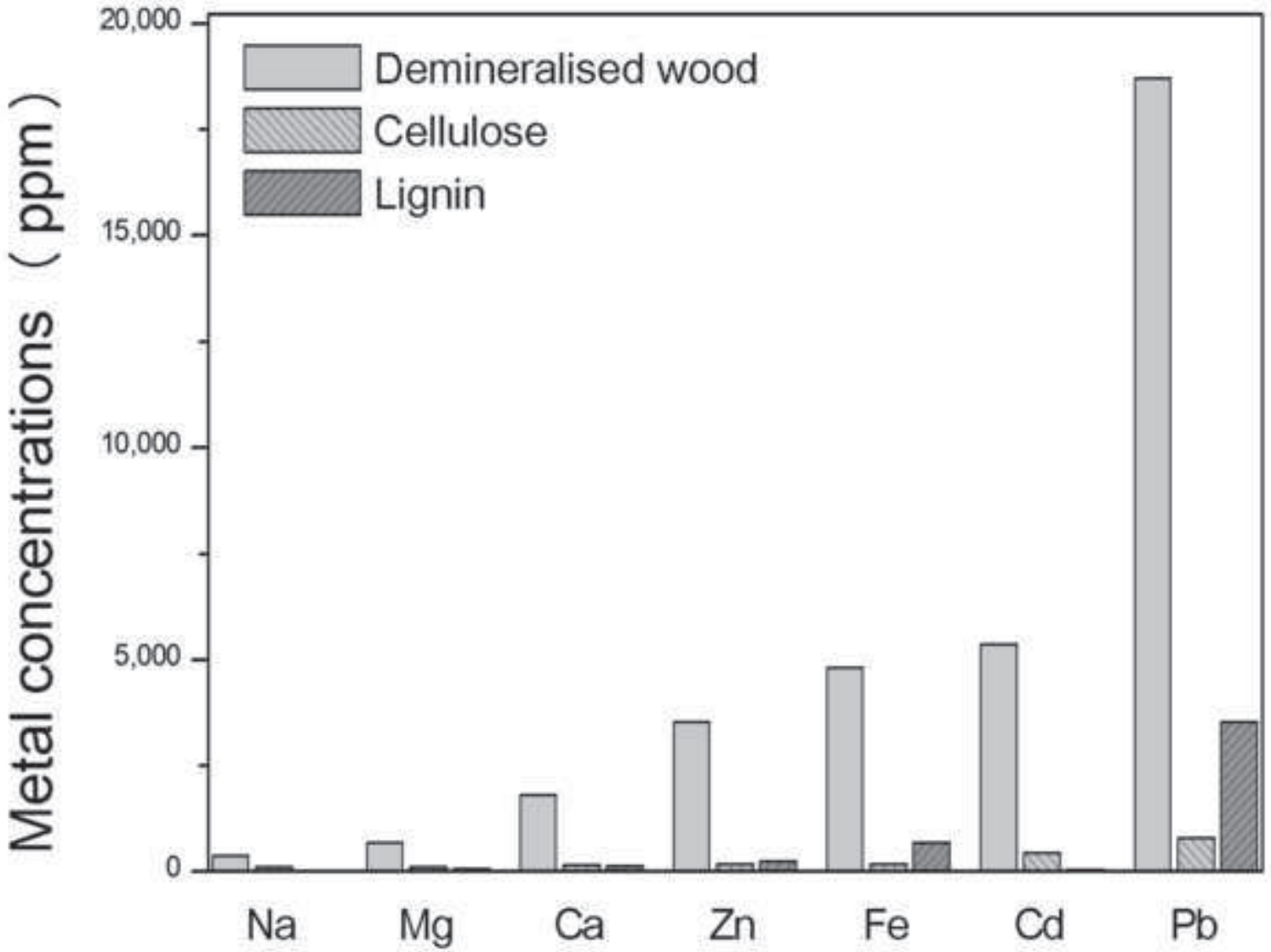

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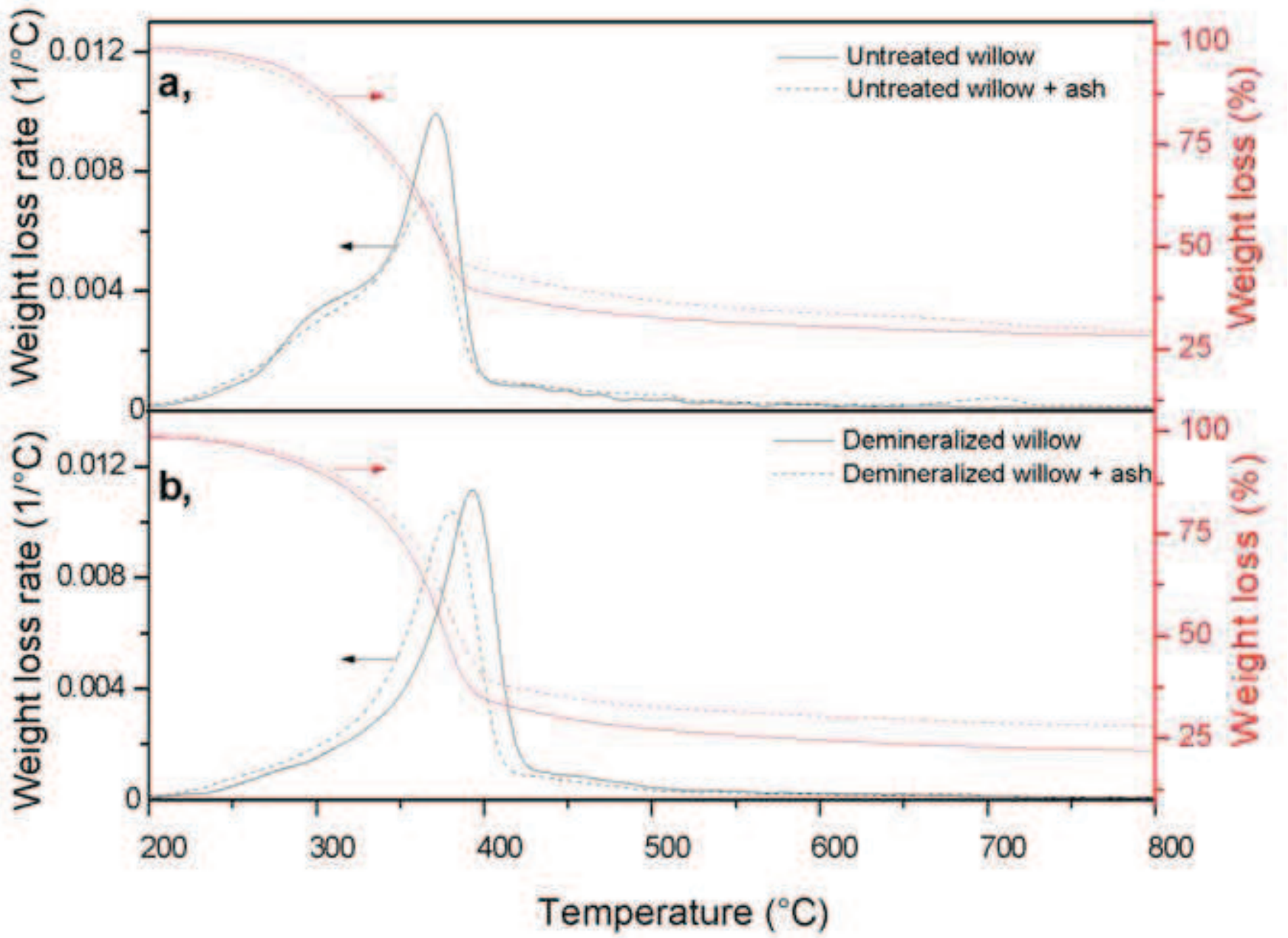

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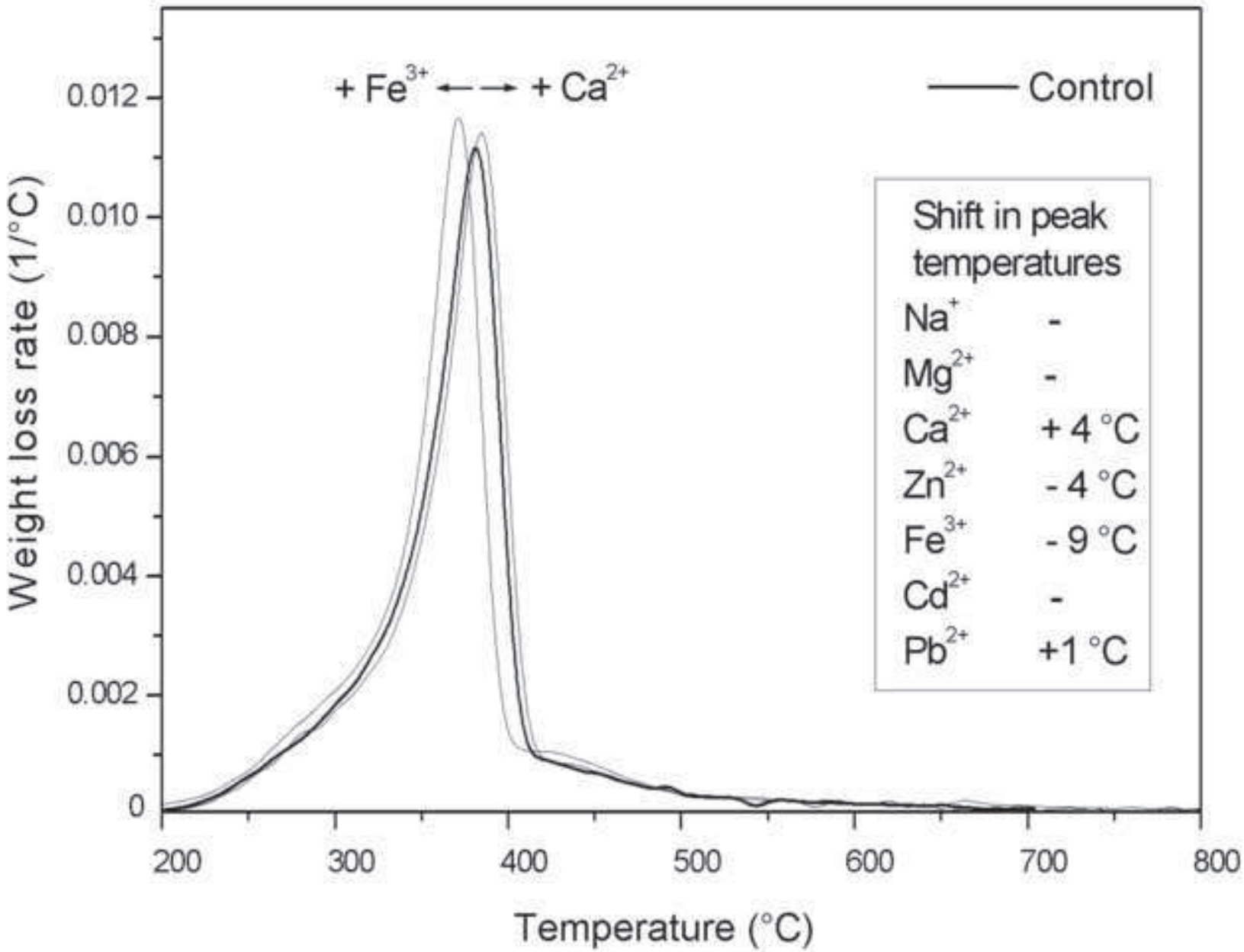

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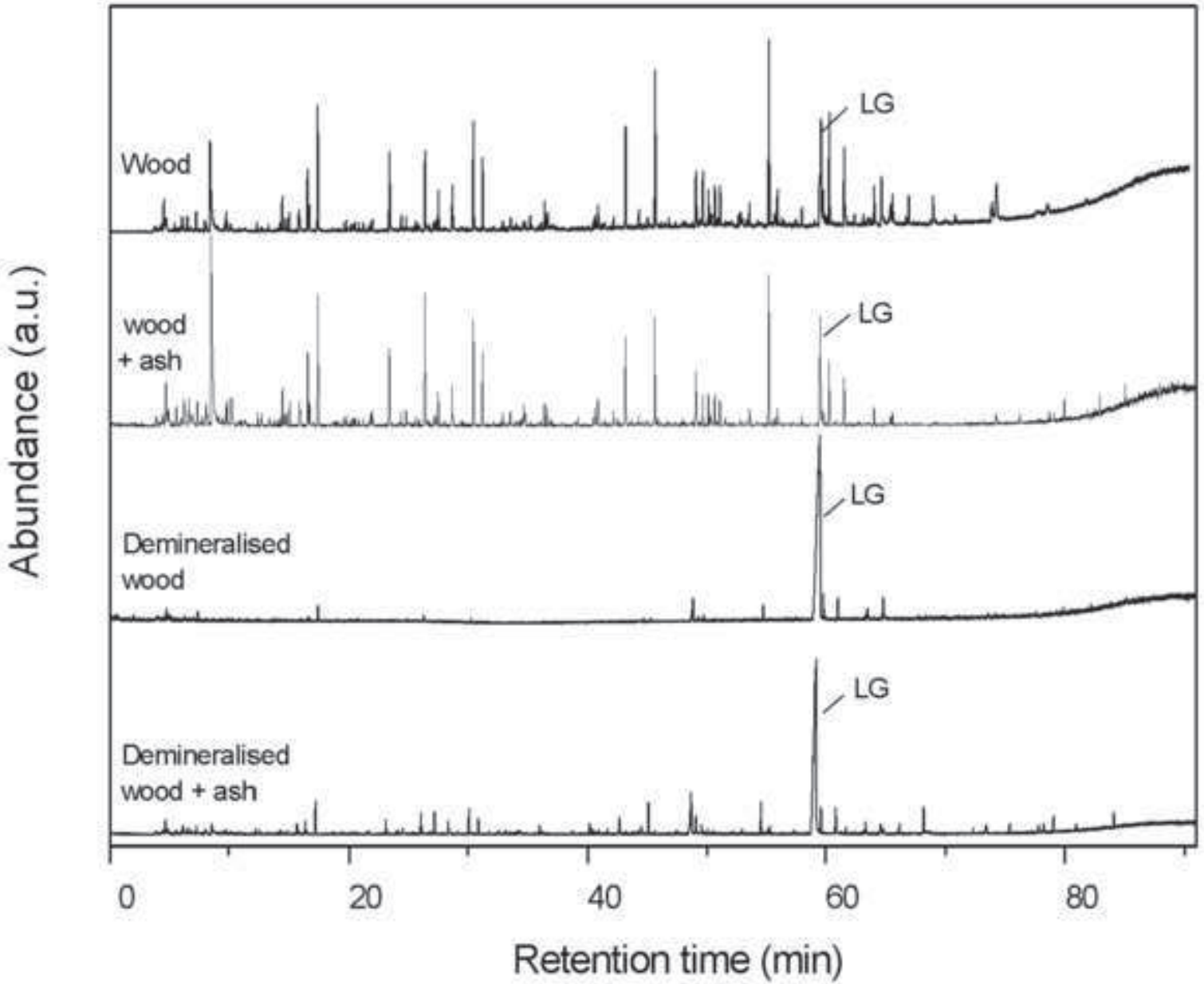

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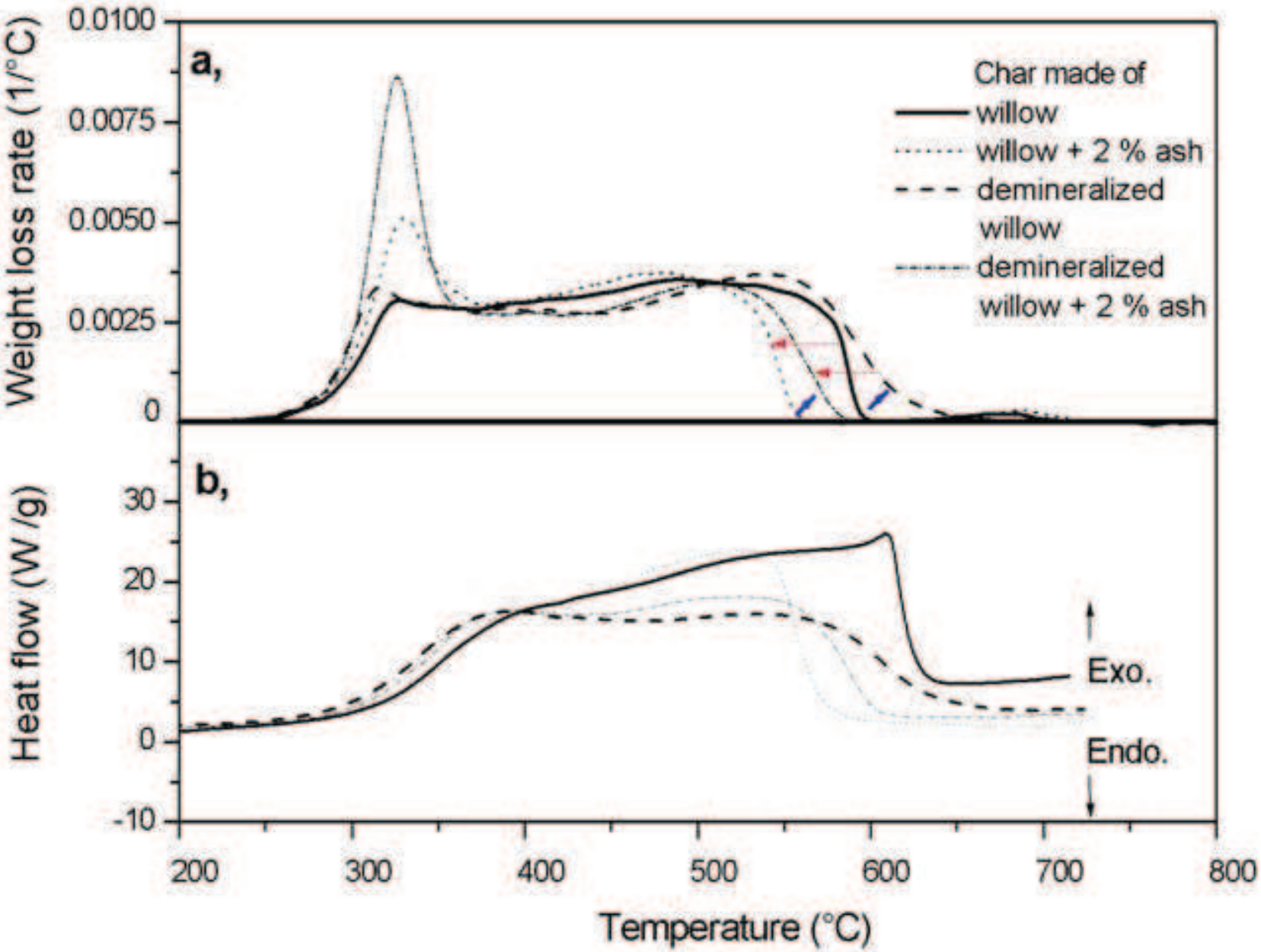

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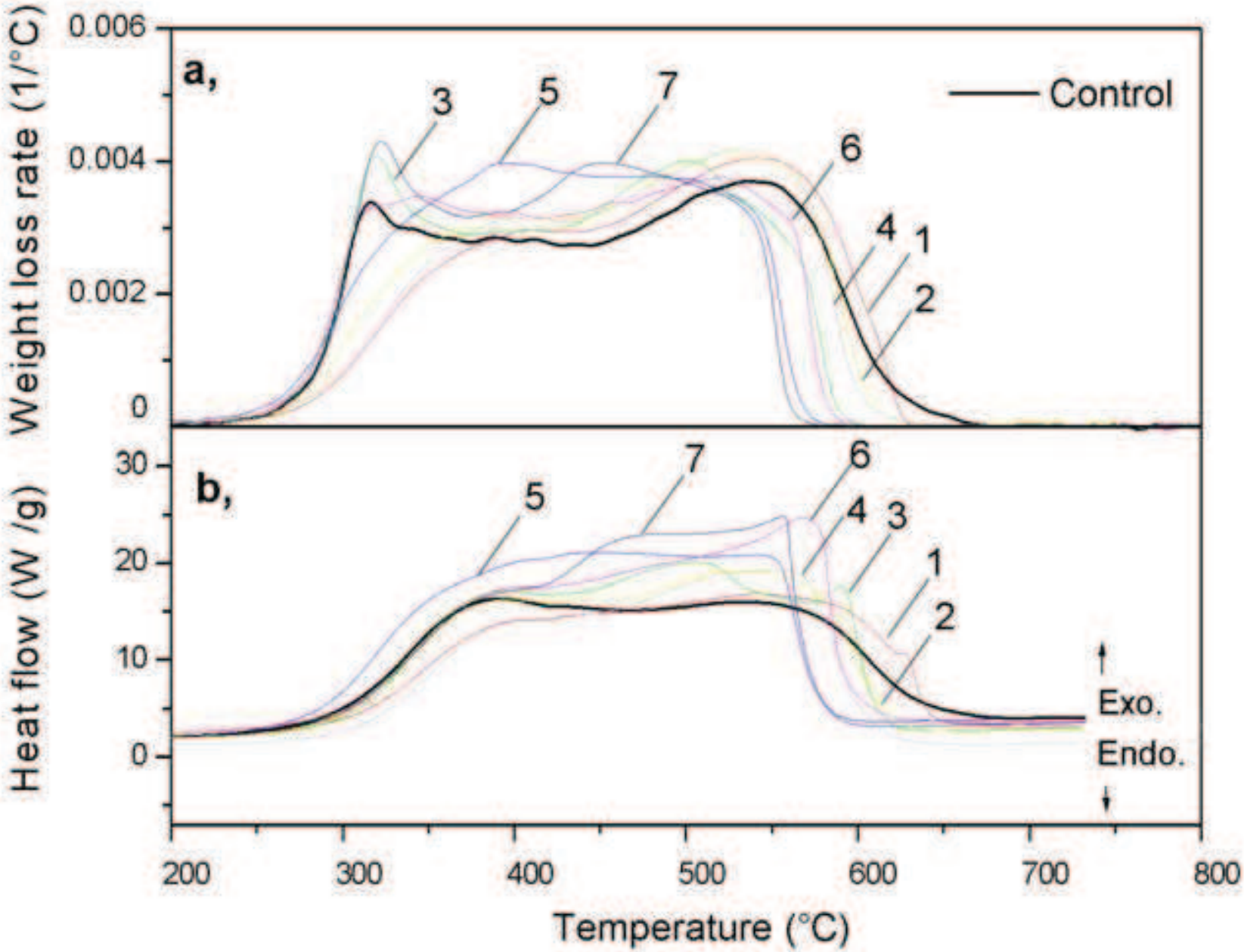
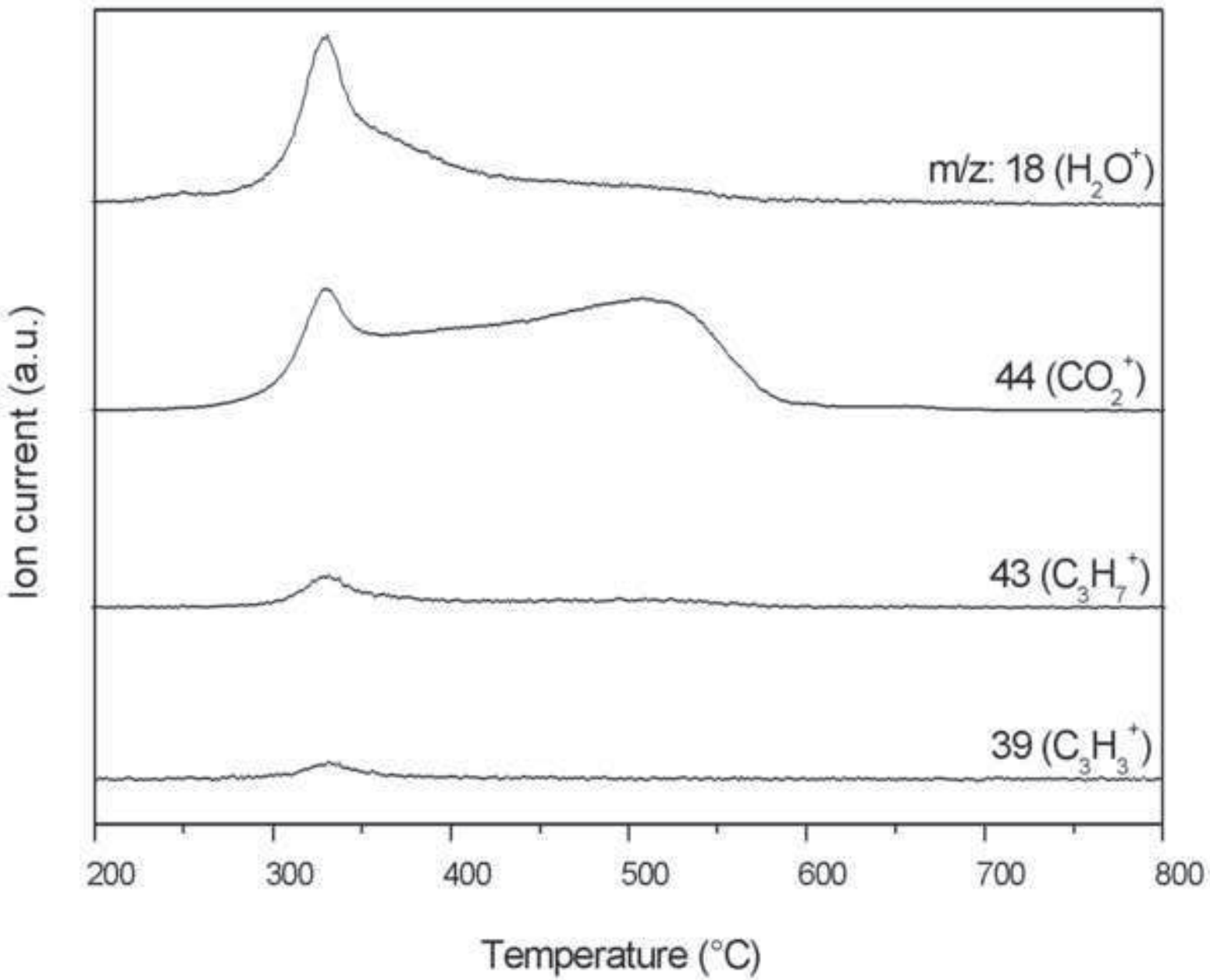
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