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A survey of the influence of biomass mineral matter in the thermochemical conversion of short rotation willow coppice

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Short rotation willow coppice (SRC) has been investigated for the influence of K, Ca, Mg, Fe and P on is pyrolysis and combustion behaviours. These metals are the typical components that appear in biomass. The willow sample was pre-treated to remove salts and metals by hydrochloric acid, and this demineralised sample was impregnated with each individual metal at the same mol/g biomass ($2.4\text{x}10^{-4}$ mol g^{-1} demineralised willow). Characterisation was performed using thermogravimetric analysis, and differential thermal analysis (DTA) for combustion. In pyrolysis, volatile fingerprints were measured by means of pyrolysis – gas chromatography – mass spectrometry (PY-GC-MS). The yields and distribution of pyrolysis products have been influenced by the presence of the catalysts. Most notably, both potassium and phosphorous strongly catalysed the pyrolysis, modifying both the yield and distribution of reaction products. Temperature programmed combustion TGA indicates that combustion of biomass char is catalysed by all the metals, while phosphorus strongly inhibits the char combustion. In this case, combustion rates follow the order for volatile release/combustion: P>K>Fe>Raw>HCl>Mg>Ca, and for char combustion K>Fe>raw>Ca~Mg>HCl>P. The samples impregnated with phosphorus and potassium were also studied for combustion under flame conditions, and the same trend was observed, i.e. both potassium and phosphorus catalyse the volatile release/combustion, while, in char combustion, potassium is a catalyst and phosphorus a strong inhibitor, i.e. K-impregnated > (faster than) raw > demineralised >> P-impregnated.

Key words: Biomass, willow SRC, pyrolysis, combustion, catalysis, metal acetates

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Introduction

Biomass and energy crops are being considered as serious options for reducing carbon dioxide emissions from electricity production. Biomass includes a vast range of materials including agricultural and forestry residues, lignocellulosic components of wastes, as well as energy crops. In the UK there are financial incentives for using biomass grown specifically for electricity production, i.e. energy crops, and this has started to develop the supply chain for, in particular, short rotation willow coppice and Miscanthus. A number of studies have examined the agronomy and the variability of these and other energy crops, in terms of "fuel quality" attributes, particularly the inorganic content.[1,2] The mix of inorganics affects the ash behaviour during combustion and this has been the subject of a number of reviews.[E.g. 3,4]

The main plant nutrients needed for energy crop production are nitrogen, phosphorus, and potassium. Other typical metals present in the fuel are Al, Ca, Fe, Mg, Na and Si. Typical ash analysis of the raw samples shows the following component: SiO_2, MgO, CaO, Al_2O_3, FeO, K_2O, P_2O_5 and indications are that these inorganics can be variable depending upon clonal variation, agronomy and geographical location.[2,5] Concentrations of ash in the range 1.4 to 3.2 wt% have been reported for Miscanthus,[1,2] and 3.2-5.1 wt% ash for SRC.[5] Similarly the main inorganic components in SRC bark clonal varieties have been reported to vary in the range 0.09-0.12 wt % P, 0.2-0.5 wt% K, 0.9-1.5 wt% Ca and 0.05-0.16 wt% Mg, while for the stems the ranges reported are lower: 0.04-0.07 wt% P, 0.1-0.2 wt% K, 0.5-0.9 wt% Ca and 0.02-0.05 wt% Mg.[5]

Pyrolysis temperature, heating rate, and biomass type are important factors influencing the volatilisation of alkali species in the biomass.[6-9] These metals together with P, S and Cl can cause ash related problems during combustion such as slagging, fouling and corrosion, and environmental problems such as the emission of volatile components.[10]

Many of the inorganic components of biomass are also known to affect the combustion behaviour of carbonaceous materials. In particular, potassium is a key metal, which not only influences ash behaviour, but also has a marked influence on pyrolysis and combustion of biomass.[9-12] Increases in char and gas yields are favoured over tar production, and the rates of both devolatilisation and char combustion increase. Iron, and particularly, potassium received a great deal of interest in the 1980's as catalysts in coal (char) gasification.[E.g. 13,14] Calcium and magnesium ores have also been of interest, because of the possibility of not only catalysing gasification, but also influencing favourably the syn-gas composition through *in situ* CO_2 absorption.[15,16] Phosphorus, another key plant nutrient, is an interesting inorganic in biomass, because it, too, influences ash chemistry, as well as the thermochemical conversion reactions. Phosphorus compounds are well-known flame-retardants, and increase char yields from textiles and woods.[17,18] They also catalyse dehydration reactions of cellulose and a recent study by Di Blasi and co-workers[19] report decreasing yields of tar products from phosphorus impregnated fir wood.

While the effects of some of the individual inorganics, K, Mg, Ca, Fe and P have been studied with respect to coal char combustion and gasification, apart from potassium there have been fewer studies for lignocellulosic material, and their *relative* importance in thermal conversion has not been considered. Consequently, this paper seeks to give an overview of the relative influence of some of the main components on the thermochemical conversion behaviour of short rotation willow coppice (SRC). The willow is demineralised by mild acid treatment and then impregnated with various inorganics inherent to biomass, potassium, phosphorous, magnesium, iron and calcium.

Experimental Section

Materials

The biomass sample of short rotation willow coppice was obtained from Rural Generation Ltd. (Londonderry, Northern Ireland). The sample was ground and sieved. The ash analysis for the oxides of Ca, Mg, Fe, K and P were as follows: CaO 36.7%; MgO 5.24%; Fe_2O_3 0.29%; K_2O 17.1%; P_2O_5 13.9%. The fraction 0.15-0.18 mm was used for demineralisation, impregnation and analyses. Magnesium acetate, ammonia phosphate, iron acetate, calcium acetate, and potassium acetate were purchased from Sigma Aldrich Company Ltd.

Sample preparation

Demineralisation. The procedure used is given by Nowakowski et al,[12] and briefly involves a hydrochloric acid treatment of the biomass sample in 2.0 M HCl at 333 K. After filtering the sample is washed with de-ionised water until the filtrate is Cl^- free . This is followed by oven drying at 333 K to constant weight. Energy Dispersive X-Ray (EDX) analysis results show that demineralization with HCl is very efficient, and metal analysis by ICP-OES indicate that Ca, Mg, Fe, and K are reduced to 119, 5.3, 7.6,<107 mg/kg (as received, after drying at 333K) respectively.[12]

Impregnation. 3 g of sample, was impregnated by potassium (as potassium acetate) to yield a 1 wt.% K-impregnated sample. In the same way 3 g of sample was impregnated by magnesium, iron, calcium and phosphorous (as the correspondent metal acetate) with equivalent mol% as the 1wt.% K-impregnated sample, i.e. each sample contains the same mol% of each inorganic species (2.4×10^{-4} mol g^{-1} demineralised willow). After addition of the corresponding acetate, the sample was moistened by 1 cm^3 of deionised water, mixed and then oven dried at 333 K to constant weight. The phosphorus impregnation was achieved using an ammonia phosphate solution prepared by neutralisation of orthophosphoric acid with ammonium hydroxide. The proximate analyses for all willow samples are given in Table 1.

Thermogravimetric analysis (TGA)

Pyrolysis test were performed in a Stanton Redcroft STA-780 DTA system. A typical sample mass of 4-5 mg was heated at 25 K min^{-1}. in a purge of nitrogen with the final temperature of 1173 K. Proximate analyses were also determined by TGA whereby the sample was first held at 383 K for 5 min, then heated at 25 K min^{-1} to 823K under nitrogen, held to constant weight, and then heated to 1173 K at 25K min^{-1} in air.

Combustion tests were also performed using the DTA analyser for both the willow samples and the char samples. A typical sample mass of 4-5 mg was heated at 25 K min^{-1} in a purge of air with the final temperature of 1173 K, and the sample was held at 1173 K for 15 min.

Analytical pyrolysis test

PY-GC-MS test were performed on each sample using a CDS 2000 pyrolyser coupled to an Agilent Technologies GC-MS gas chromatograph. The column was a RTX 1701 (14% cyanopropylphenyl, 86% dimethylpolysiloxane, 61.3 m 0.25 mm id., 0.25μm). The gas chromatograph oven was held at 313 K for 2 min and then programmed at 4 K min^{-1} to 513 K, held for 30 min. Approximately 2.5 mg of sample was placed in 20 mm quartz tube in between quartz wool. The sample was pyrolysed at a set point temperature of 900 K at a ramp rate of 1 K ms^{-1} with the final dwell time of 20 s.

Suspended particle combustion studies in a Meker burner

Combustion studies on suspended biomass particles were conducted using a Meker burner. A detailed approach for the single particle combustion experiments was described by Jones et al.[9] Natural gas was used and the stoichiometry controlled so that the part of the flame in which the particles were placed reached a temperature of 1500 K. The oxygen content at this location was 2.75 mol%. The particles (ca. 3 mm in length, 1 ± 0.2 mg) are held in place on either a steel or quartz needle adjacent to a R-type thermocouple in a ceramic housing. A water-cooled probe surrounds both the particle and the thermocouple before entry into the flame. The probe is placed into the flame ensuring that the particle and thermocouple are located centrally above the burner. The water-cooled sleeve is then retracted so that the particle and thermocouple are exposed to the flame. Upon completion of particle combustion, the water-cooled sleeve is slid back over the needle and thermocouple and the unit is removed from the flame. A Photo-Sonics Phantom V7 high-speed video system was used to record the images of the combusting particles at a speed of 1000 frames per second (fps), during both sets of experiments.

Results and Discussion

TGA pyrolysis.

Differential thermogravimetric (DTG) result comparing the influence of the different inorganics on the pyrolysis of the willow SRC are shown in Fig. 1(a) for raw willow, HCl treated willow (demineralised) and potassium and phosphorous impregnated willow, and in Fig. 1(b) for raw willow, HCl treated willow and iron, calcium and magnesium impregnated willow. DTG analyses of the SRC raw willow revealed its thermal degradation occurs in two steps. Hemicellulose, cellulose and lignin, the basic biomass components, decompose thermochemically in the following temperature ranges: 423-623 K, 548-623 K and 523-773K respectively.[20,21] The first step of thermal degradation is attributed to the decomposition of hemicellulose and the initial stage of degradation of cellulose, while the second step is attributed to the degradation of lignin and the final degradation of cellulose.[12] The main peak maximum temperatures are also labelled. Fig 1a and 1b shows that after acid treatment the first peak becomes much weaker indicating that the acid treatment not only removes metals from the SRC but also digests the hemicellulose to some extent. Also, after acid treatment, the second main peak shifts to a slightly higher temperature; this shows that some catalytic species have been removed by acid washing. In Fig 1(a) it is seen that both potassium and phosphorous strongly catalyse the degradation, as demonstrated by the large shift to lower temperature of the main decomposition peak for these impregnated samples. Fig 1(b) compares the influence of the other metals in pyrolysis. It is clear that these metals have very little influence on the thermal decomposition under pyrolysis conditions; a very small shift to lower temperature is seen for the main peaks in the profiles for the Mg and Fe impregnated samples, while no effect of Ca is apparent.

The impact of the metals on the volatile and fixed carbon yields are shown in Table 1. As note previously, demineralisation increases the volatile yield, while the presence of potassium decreases the volatile yield. Iron, potassium and phosphorus increase the fixed carbon yield, and this is especially noticeable for the P-impregnated willow sample. Interestingly, magnesium and calcium both decrease the fixed carbon content.

PY-GC-MS test.

Pyrolysis – gas chromatography – mass spectrometry (PY-GC-MS;) analysis has been introduced to study the generation of light to medium volatiles produced during pyrolysis of the treated willow samples. The results are given in Fig. 2, for the HCl treated Fe, and K impregnated willow samples, and in Fig. 3 for the P-impregnated sample. Other impregnated willow samples yielded similar chromatograms to that produced by pyrolysis HCl treated willow, and so are not shown. The main peaks were tentatively assigned from mass spectral detection and from the literature[22-24] and from the mass spectrometry library (NIST 05) and are given under each figure.

Previous work[9,11,12,25,26] has shown the catalytic effect inorganic metals, in particular potassium, have during pyrolysis and their impact in the alteration of thermal decomposition mechanisms. The reported influence of potassium on pyrolysis is corroborated here whereby promotion of heterolytic depolymerization and fragmentation to low molecular weight components (e.g. acetic acid, formic acid, glyoxal, hydroxyacetaldehyde and acetol) occurs at the expense of levoglucosan and other anhydrosugars. Studying the fingerprint of pryolysis products produced in the presence of other metals reveals some minor changes in product distributions, but no obvious influence on the anhydrosugars. In contrast, the pyrolysis fingerprint of willow in the presence of phosphorus is very different and a simpler product distribution is seen, with levoglucosenone and furfural as major components. These products have been observed during the decomposition of fir wood[19] and Miscanthus[27] when impregnated with phosphorus salts. In the presence of phosphorus, levoglucosenone is a major product from the cellulose component of the cell wall,[27-29] while furfural arises from both cellulose and hemicellulose components.[27]

DTG Combustion.

Differential thermogravimetric (DTG) result comparing the influence of the different inorganics on the combustion of willow are shown in Fig. 4(a) for raw willow, willow HCl treated, potassium, and phosphorous impregnated willow and in Fig. 4(b) for raw willow, willow HCl treated, iron, calcium and magnesium impregnated willow. The first (main) peak in these figures represents volatile release, ignition and combustion, while the second, broader peak is a result of the slower char combustion stage. In these Figures it is seen that potassium, phosphorous and iron strongly catalyses the volatile release stage as seen in the shift to lower temperature of the first (main) peak. Upon demineralisation (HCl treated sample) the char combustion stage becomes very slow, relative to the raw SRC, and a broad char combustion peak is apparent. Addition of potassium, iron, calcium and magnesium all results in a shift to lower temperature of the char combustion peak, indicative of catalysis. In the case of potassium a sharp char combustion peak is present demonstrating a fast, exothermic catalysed char combustion stage. Phosphorus is seen to inhibit char combustion and the final burn-out temperature for the P-impregnated willow is greater than for the demineralised sample. Thus for the low heating-rate temperature programmed combustion experiments, combustion rates follow the order for volatile release/combustion: P>K>Fe>Raw>HCl>Mg>Ca, and for char combustion K>Fe>raw>Ca~Mg>HCl>P.

Impact of P and K in combustion

The potassium and phosphorus impregnated samples were studied in more detail using a high temperature combustion experiment developed previously.[9] Observations of videos and still images for the Meker burner experiments showed differences in the combustion behaviours of willow samples. **Figure 5** shows close-up images of different doped particles during the combustion experiments. Different stages of single particle combustion were distinguished and visually analysed, in order to characterise the differences in combustion properties of the willow samples (raw, demineralised, potassium and phosphorus impregnated. The onset of volatile combustion was observed as either a flame above the particle and/or the appearance of radiation around the particle. The end of volatile combustion was marked by the disappearance of this. The start of char burn-out was characterised as the bottom part of the particle beginning to radiate red/orange. Often, at the same time, the top of the particle was still undergoing volatile combustion. The end of char burn-out was characterised as the point at which the particle ceased to decrease in size, and a 'boiling' drop of melted ash observed.

For both the demineralised and potassium impregnated particles, volatile combustion can be identified by a flame above or around particle. It is also seen that the char combustion starts simultaneously with the volatile combustion, which is evidenced by the lower end of particle starting to glow while the volatile flame is still present. For the phosphorus impregnated sample, volatile combustion lasts for a very short time and the volatile combustion flame is not very luminous compared to the potassium impregnated or demineralised samples. Upon the disappearance of the volatile combustion flame, char burn-out reaction begins identified by radiation from the whole particle, and during this stage the particle integrity is retained up to the end of the combustion reaction. At the end of the combustion, the particle shrinks more rapidly and ash is left attached to the supporting needle. As reported by Jones[9] for the demineralised sample devolatalisation proceeds by the appearance of black boiling tar, this coats the entire particle very rapidly. As the tar starts to evaporate a bright flame occurs above the particle. The particle decreases in size considerably and the combustion resembles tar/oil combustion rather then solid fuel combustion. After the volatile combustion stage the remaining particle starts to glow and shrinkage of the particle occurs, but much more slowly than that for the potassium impregnated sample. For phosphorus impregnated willow, the char combustion reaction is identified by radiation from the entire particle and occurs the slowest of the three treatment. This stage can lasts up to 30 seconds for a 1 mg particle.

Some observations of the duration of the volatile combustion and char burn-out stages were made. Results presented in **Figure 6 (a)** (volatile combustion) and **Figure 6(b)** (char combustion) are average times for particles of mass 1 ± 0.2 mg.

Volatile combustion follows the sequence: P-impregnated < K-impregnated < demineralised ≤ raw and indicates a catalytic impact of both additives on this stage of decomposition. Observation for char burn-out duration shows that phosphorus inhibits this stage while potassium shows a catalytic role. The char combustion follows the sequence: K-impregnated > (faster than) raw > demineralised >> P-impregnated.

Conclusions.

Short rotation willow coppice (SRC) has been investigated for the influence of K, Ca, Mg, Fe and P on is pyrolysis and combustion behaviours. Demineralised willow (HCl treated) was impregnated with the metal acetate salts and ammonium phosphate solution respectively. Both potassium and phosphorous strongly catalyse the pyrolysis, modifying both the yield and distribution of reaction products. The metals, Mg and Fe, have a very small catalytic influence on the rate of pyrolysis as seen in TGA experiments, while no effect is seen upon Ca impregnation. Iron, potassium and particularly phosphorus increase the fixed carbon yield, while magnesium and calcium both decrease the fixed carbon contents. Pyrolysis-GC-MS results show that potassium and phosphorus have the largest influence on tar composition. Potassium promotes heterolytic decomposition and fragmentation to low molecular weight components (e.g. acetic acid, formic acid, glyoxal, hydroxyacetaldehyde and acetol) occurs at the expense of levoglucosan and other anhydrosugars. In contrast, phosphorus promoted decomposition yields a simplified product distribution with levoglucosenone and furfural as major components

Temperature programmed combustion TGA indicates that potassium, phosphorous and iron strongly catalyses the volatile release stage as seen in the shift to lower temperature of the first (main) peak. Also, potassium, iron, calcium and magnesium all results in a shift to lower temperature of the char combustion peak, indicative of catalysis. Phosphorus is seen to inhibit char combustion. For the low heating-rate temperature programmed combustion experiments, combustion rates follow the order for volatile release/combustion: P>K>Fe>Raw>HCl>Mg>Ca, and for char combustion K>Fe>raw>Ca~Mg>HCl>P.

The samples impregnated with phosphorus and potassium were also studied for combustion under flame conditions, and the same trend was observed, i.e. both potassium and phosphorus catalyse the volatile release/combustion, while, in char combustion, potassium is a catalyst and phosphorus a strong inhibitor. In this case, the char combustion follows the sequence: K-impregnated > (faster than) raw > demineralised >> P-impregnated.

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Table captions

Table 1: Analyses of willow samples (as received)

Figures captions

Figure 1: DTG pyrolysis profiles for willow SRC samples.

Figure 2: Pyrolysis-GC-MS chromatogram for: a) HCl treated willow sample, b) iron impregnated willow sample, c) potassium impregnated willow sample

Figure 3: Pyrolysis-GC-MS chromatogram for phosphorus impregnated willow.

Figure 4: Temperature programmed combustion: burning profiles for impregnated willow samples

Figure 5. Close-up images of particles illustrating different physicochemical changes occurring in the combustion of (a) demineralised willow, (b) potassium impregnated willow and (c) phosphorus impregnated willow.

Figure 6. Average durations for single particles (1 ± 0.2 mg) of willow of (a) volatile combustion and (b) char combustion

Table 1: Analyses of willow samples (as received).

Sample	Moisture (wt%)	Ash (wt%)	Fixed carbon (wt%)	Volatiles (wt%)
Willlow raw	4.4	3.3	18.0	74.3
Willow HCl treated	4.4	2.6	16.5	76.5
Willow K-impregnated	4.6	4.2	18.9	72.3
Willow Mg-impregnated	4.4	4.0	15.4	76.2
Willow Fe-impregnated	2.7	3.4	18.9	75.0
Willow Ca-impregnated	7.6	4.0	15.2	73.2
Willow P-impregnated	5.5	6.2	24.5	63.8

Proximate measure by TGA at 1173.15 K

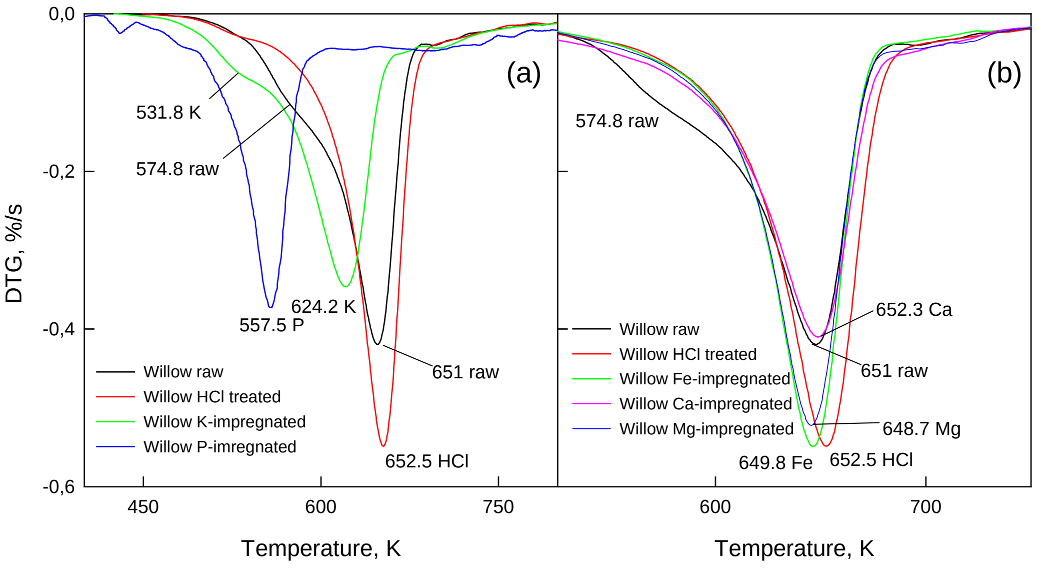

Figure 1: DTG pyrolysis profiles for willow samples.

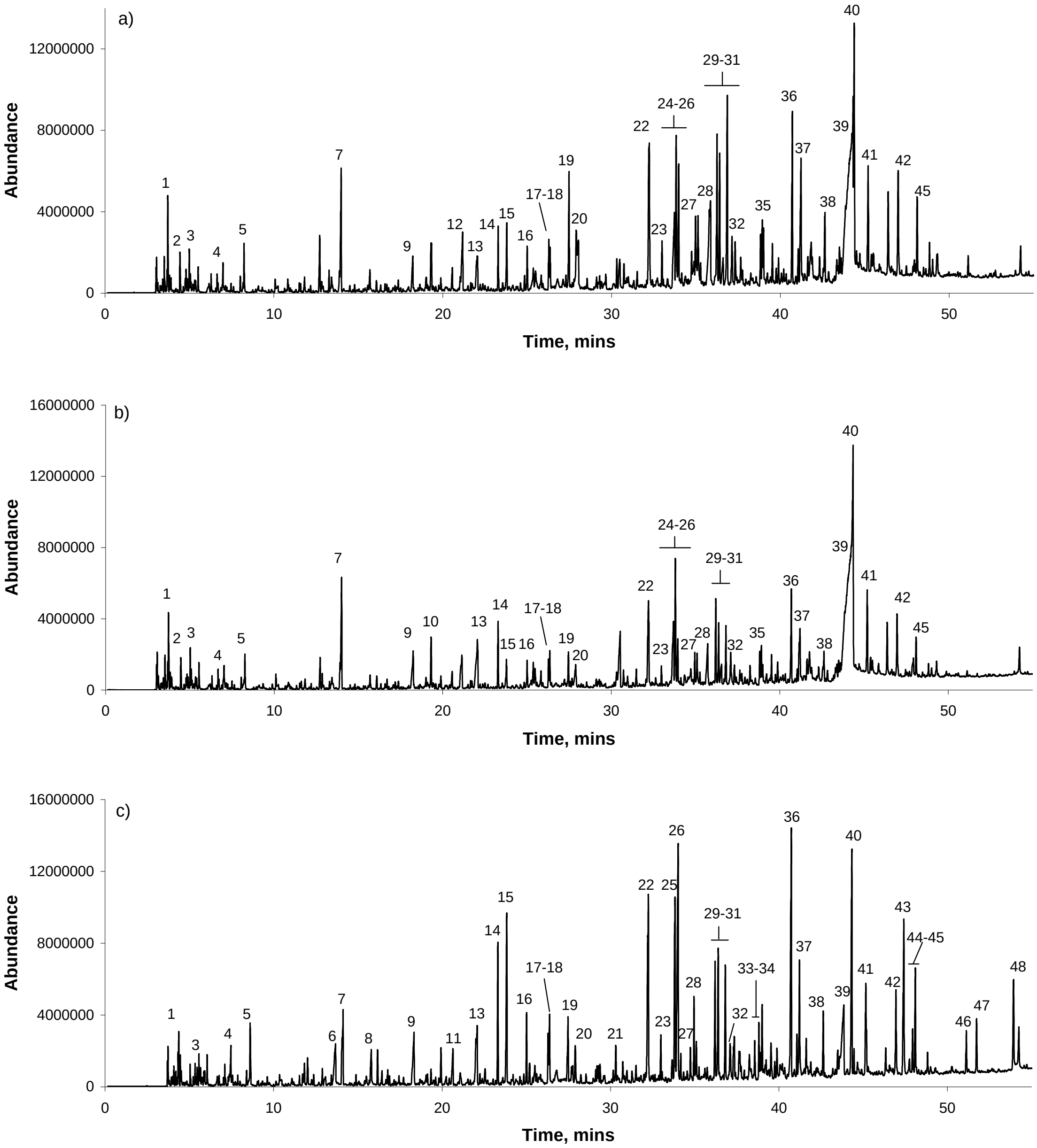

Figure 2: Pyrolysis-GC-MS chromatogram for a) HCl treated willow sample, b) iron impregnated willow sample, c) potassium impregnated willow sample.

The main peaks are assigned as follows: 1: 2-propenal; 2: 2-methyfuran; 3: 2-butenone; 4: acetic acid; 5: toluene; 6: 2-cyclopenten-1-one; 7: furfural; 8: 2-furanmethanol; 9: 1,2-cyclopentanedione; 10: 2,3-dimethylpentanal; 11: 2(5h)-furanone; 12: 5-methyl-2-furancarboxaldehyde; 13: 2-hydroxy-3-methyl-2-cyclopenten-1-one; 14: phenol; 15: guaiacol; 16: 2-methylphenol; 17: 4-methylphenol; 18: 3-methylphenol; 19: 4-methylguaiacol; 20: 2,4-dimethylphenol; 21: 4-ethylguaiacol; 22: 4-vinylguaiacol; 23: eugenol; 24: 5-hydroxymethylfurfural; 25: 1,2-benzenediol; 26: syringol; 27: 3-methyl-1,2-benzenediol; 28: 3,4-dimethoxyphenol; 29: 4-methyl-1,2-benzenediol; 30: iso-eugenol; 31: 1,2,4-trimethoxybenzene; 32: vanillin; 33: 2-methyl-1,4-benzenediol; 34: 4-ethylcatechol; 35: 3,5-dimethoxyacetophenone; 36: 1,2,3-benzenetriol; 37: methoxyeugenol; 38: methoxyeugenol; 39: levoglucosan; 40: methoxyeugenol; 41: syringaldehyde; 42: acetosyringone; 43: 4-((1e)-3-hydroxy-1-propenyl)-2-methoxyphenol; 44: 4-hydroxy-2-methoxycinnamaldehyde; 45: desaspidinol; 46: homosyringic acid; 47: 2-pentanone, 1-(2,4,6-trihydroxyphenyl); 48: 4-ethoxy-2,5-dimethoxybenzaldehyde.

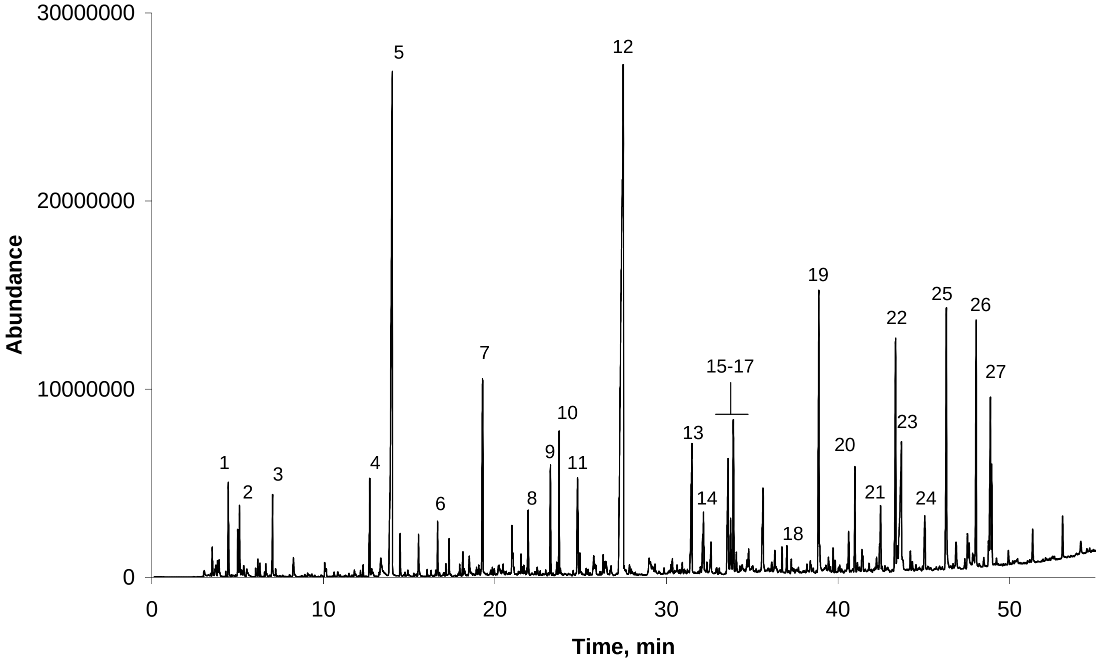

Figure 3: Pyrolysis-GC-MS chromatogram for phosphorus impregnated willow.

The main peaks are assigned from mass spectral detection as follows: 1: 2-methylfuran; 2: 2-butanone; 3: acetic acid; 4: 2(5H)-furanone; 5: furfural; 6: 2-acetylfuran; 7: 5-methylfurfural; 8: 2-hydroxy-3-methyl-2-cyclopenten-1-one; 9: phenol; 10: guaiacol; 11: methyl 2-furoate; 12: levoglucosenone; 13: 1,4;3,6-dianhydro-α-d-glucopyranose; 14: 4-vinylguaiacol; 15: 5-hydrxoymethylfurfural; 16: 1,2-benzenediol; 17: syringol; 18: vanillin; 19: 4-propylguaiacol; 20: guaiacylacetone; 21: 2,4'-dihydroxy-3'-methoxyacetophenone; 22: *unassigned;* 23: levoglucosan; 24: syringaldehyde; 25: homosyringic acid; 26: 1-(2,4,6-trihydroxyphenyl)-2-pentanone; 27: aspidinol.

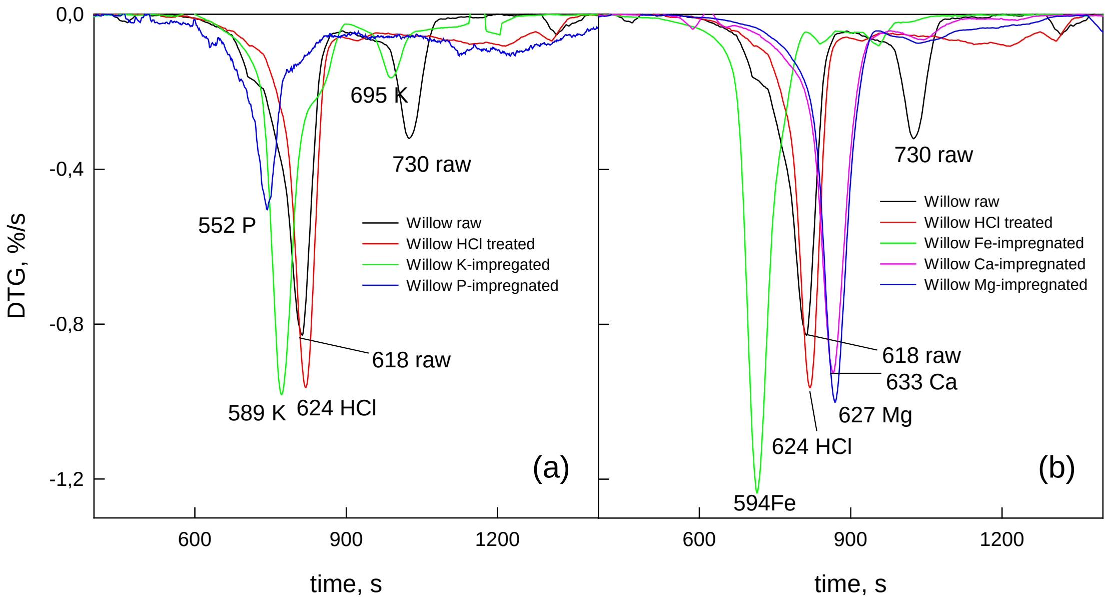

Figure 4: Temperature programmed combustion: burning profiles for impregnated willow samples

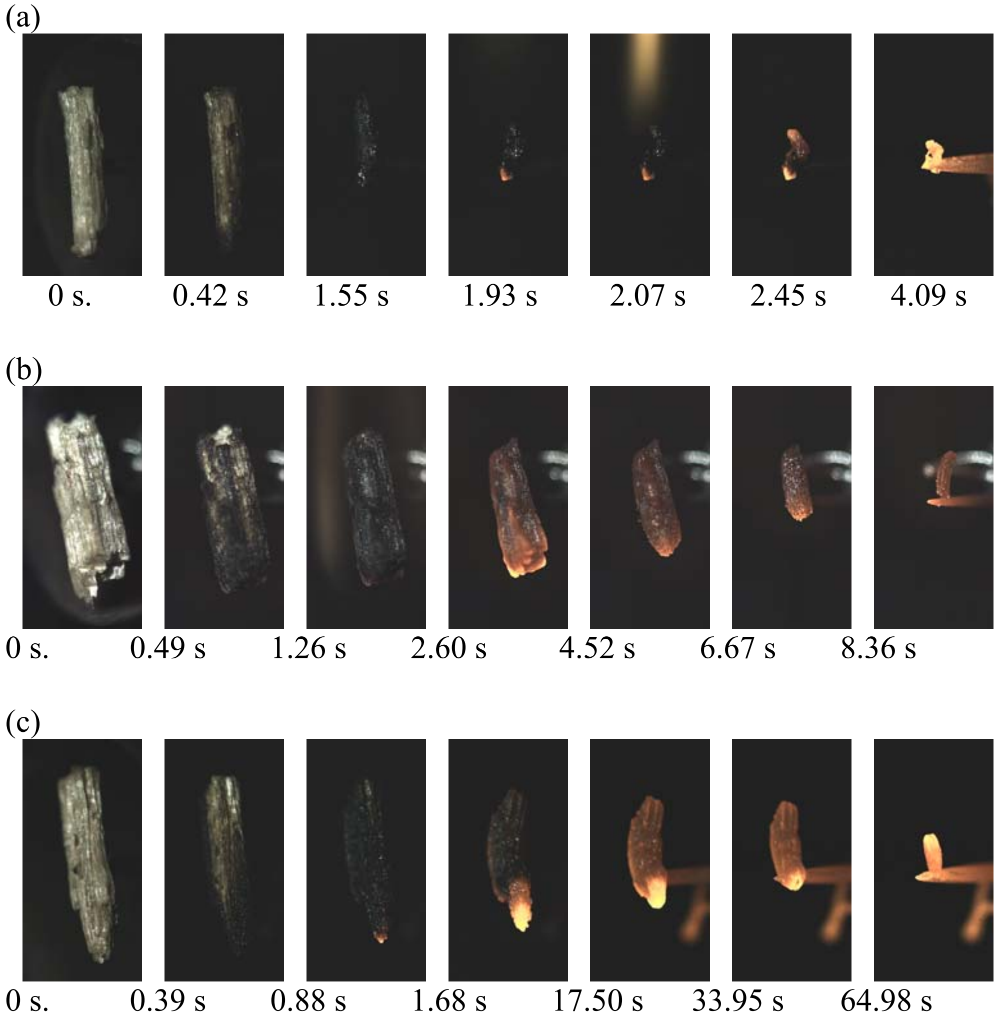

Figure 5. Close-up images of particles illustrating different physicochemical changes occurring in the combustion of (a) demineralised willow, (b) potassium impregnated willow and (c) phosphorus impregnated willow.

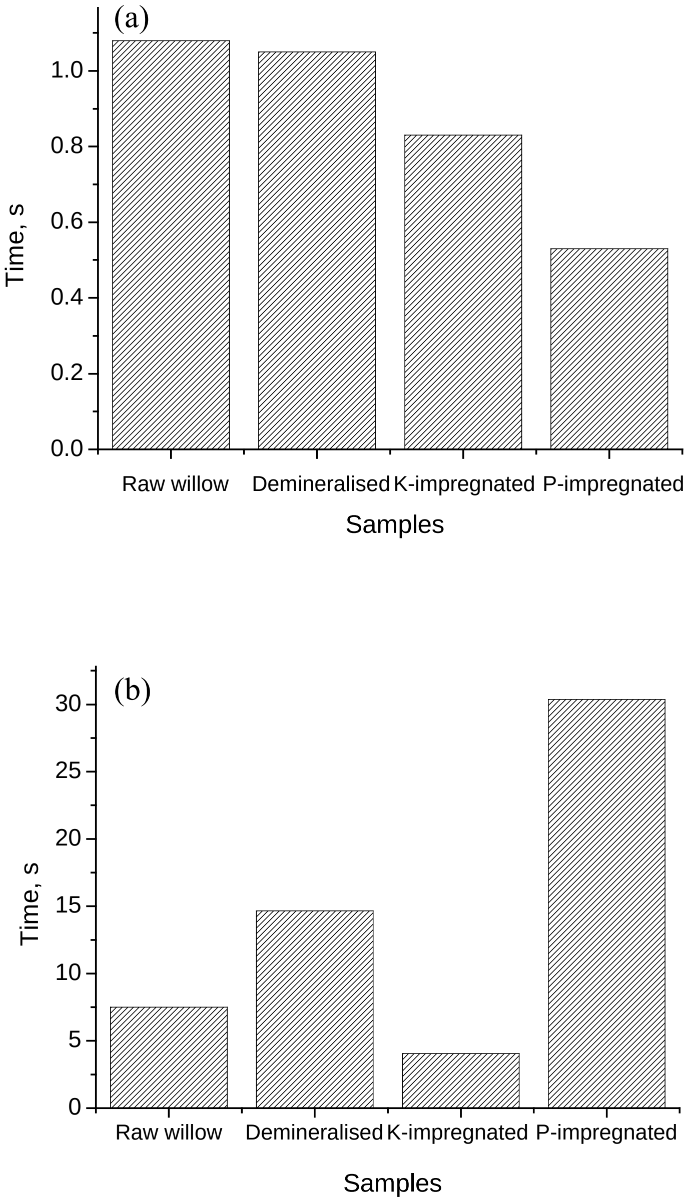

Figure 6. Average durations for single particles (1 ± 0.2 mg) of willow of (a) volatile combustion and (b) char combustion