

## Phosphorus catalysis in the pyrolysis behaviour of biomass

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### ABSTRACT

Phosphorus is a key plant nutrient and as such, is incorporated into growing biomass in small amounts. This paper examines the influence of phosphorus, present in either acid ( $\text{H}_3\text{PO}_4$ ) or salt ( $(\text{NH}_4)_3\text{PO}_4$ ) form, on the pyrolysis behaviour of both *Miscanthus × giganteus*, and its cell wall components, cellulose, hemicellulose (xylan) and lignin (Organosolv). Pyrolysis–gas chromatography–mass spectrometry (PY–GC–MS) is used to examine the pyrolysis products during thermal degradation, and thermogravimetric analysis (TGA) is used to examine the distribution of char and volatiles. Phosphorus salts are seen to catalyse the pyrolysis and modify the yields of products, resulting in a large increase in char yield for all samples, but particularly for cellulose and *Miscanthus*. The thermal degradation processes of cellulose, xylan and *Miscanthus* samples occur in one step and the main pyrolysis step is shifted to lower temperature in the presence of phosphorus. A small impact of phosphorus was observed in the case of lignin char yields and the types of pyrolysis decomposition products produced. Levoglucosan is a major component produced in fast pyrolysis of cellulose. Furfural and levoglucosenone become more dominant products upon P-impregnation pointing to new rearrangement and dehydration routes. The P-catalysed xylan decomposition route leads to a much simpler mixture of products, which are dominated by furfural, 3-methyl-2-cyclopenten-1-one and one other unconfirmed product, possibly 3,4-dihydro-2-methoxy-2H-pyran or 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one. Phosphorus-catalysed lignin decomposition also leads to a modified mixture of tar components and desaspidinol as well as other higher molecular weight component become more dominant relative to the methoxyphenyl phenols, dimethoxy phenols and triethoxy benzene. Comparison of the results for *Miscanthus* lead to the conclusion that the understanding of the fast pyrolysis of biomass can, for the most part, be gained through the study of the individual cell wall components, provided consideration is given to the presence of catalytic components such as phosphorus.

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### 1. Introduction

Phosphorus is one of the key plant nutrients, and as such, has variable concentrations in biomass and energy crops [1]. It is an interesting element in fuels, since, like potassium, it influences not only the thermal behaviour [2] but also the ash behaviour is combustion systems [3]. A typical concentration of  $\text{P}_2\text{O}_5$  in the ash of willow is 11.5% [4], while values are lower for the grasses, of the order of 2–4% [4,5]. A value of 5.3%  $\text{P}_2\text{O}_5$  in the ash has been reported previously for *Miscanthus × giganteus* [4]. The mobilization and ash behaviour of phosphorus during combustion is a topic generating

interest since it impacts not only on slagging, corrosion and emissions, but also on sustainability and the possible beneficial use of ash residues [6,7].

Phosphorus compounds are well-known flame-retardants, and increase char yields from textiles and woods [8,9]. They also catalyse dehydration reactions of cellulose and a recent study by Di Blasi et al. [10] report decreasing yields of tar products from phosphorus impregnated fir wood. There has been some previous work examining the mechanism of phosphoric acid catalysed decomposition of biomass, particularly cellulose [11,12]. Dobelet et al. [11] used analytical pyrolysis combined with gas chromatography to study the composition of volatile products of different celluloses impregnated with various amounts of phosphoric acid. The influence on the yields of levoglucosan and levoglucosenone was studied taking into account the supramolecular structure, degree of polymerization, hydrophilic properties and pre-treatment conditions of the celluloses. It was found that levoglucosenone predominates in the volatiles of acid

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catalysed pyrolysis. However, the relative total amount of both 1,6-anhydrosaccharides varied only in a narrow range of 75–85% regardless of the impregnation and pre-treatment conditions of the celluloses. For pulps with a less ordered cellulosic supramolecular structure, breaking of glycosidic bonds with the formation of levoglucosan besides levoglucosenone occurred and the relative amount of non-dehydrated anhydrosaccharides increased. Dobelet al. [12] also studied the influence of phosphoric acid pre-treatment of biomass materials (beech wood sawdust, recycled Kraft pulp, newsprint, microcrystalline cellulose Thermocell) on the pyrolysis products yields. Birch wood treated with 1% phosphoric acid yields approximately 15% of levoglucosan and 8% levoglucosenone. At higher concentrations of phosphoric acid (2.5%) the formation of more levoglucosenone (17%) was observed. These authors presented a mechanism of acid catalysed splitting of glycosidic bonds in cellulose, showing that the interaction of mineral acids proceeds via protonation of the oxygen atom on glycosidic bonds, stabilisation of the pyranosyl cation by mesomerism, the formation of oxonium ions by water addition, and stabilisation of the hydrogen splitting.

The aims of the present work are to examine the influence of both phosphoric acid and ammonium phosphate on the products from pyrolysis of other cell wall components, hemicellulose (xylan) and lignin (Organosolv). Results are compared with the analogous cellulose decomposition routes. A second aim is to examine how well the pyrolysis of an energy crop, *Miscanthus × giganteus*, can be described in terms of the pyrolysis of its cell wall components.

## 2. Experimental

### 2.1. Materials

The following cell wall components: cellulose, hemicellulose (oat spelt xylan) and lignin (Organosolv) were used in this study. All compounds were purchased from the Sigma–Aldrich Company Ltd. The biomass sample of *Miscanthus × giganteus* was obtained from Rothamsted Research (Harpenden, Hertfordshire, UK). The sample was ground and sieved. The fraction 0.15–0.18 mm was used for demineralisation, impregnations and analyses. The cell wall components of *Miscanthus × giganteus* were determined using a combination of methods from the literature [13–15]. The biomass sample was first extracted by soxhlet extraction with a mixture of 95% ethanol and toluene (1:2 v/v) for 6 h followed by 95% ethanol for 4 h and then distilled water for 2 h. This yielded the extractives content on the basis of the sample weight loss. Lignin content was determined as Klason lignin, calculated as the weight loss after 72% sulphuric acid treatment of the extractive free sample. Holocellulose samples were prepared by delignification using acid chlorite, where sodium chlorite was used for the reaction in acetate buffer (pH = 3.5). Hemicellulose was removed by alkali extraction with 17.5% NaOH solution. The analysis was as follows on a dry ash free basis: Extractives, 5.11%; Klason lignin, 17.34%; Cellulose, 51.26%; Hemicellulose, 26.29%.

### 2.2. Sample preparation

#### 2.2.1. Demineralisation

Hydrochloric acid treatment of cellulose and lignin sample was performed by heating of 10 g of sample in 50 cm<sup>3</sup> of 2.0 M HCl for 6 h at 333 K. After 48 h the sample, left in the HCl solution, was again heated at 333 K for 6 h. The sample was filtered, then washed using de-ionized water until the filtrate was Cl<sup>-</sup> free (checked by 0.1 M silver nitrate solution). The sample was then oven dried at

333 K to constant weight. The same procedure was applied for *Miscanthus* biomass sample.

#### 2.2.2. Impregnation

**2.2.2.1. Ortho-phosphoric acid. H<sub>3</sub>PO<sub>4</sub> – impregnation:** 0.5 g of sample (demineralised cellulose, lignin and *Miscanthus* as well as raw xylan from oat spelt), analysed before impregnation for moisture content, was impregnated by phosphorus to yield a 2 wt.% P-impregnated sample. 0.1 M solution of ortho-phosphoric acid was used for impregnation. After addition of phosphorus acetate the sample was moistened by approximately 5 cm<sup>3</sup> of de-ionized water, mixed and then oven dried at 333 K to constant weight. *Please note:* H<sub>3</sub>PO<sub>4</sub> impregnated samples in text are called ‘acid impregnated’ samples.

**2.2.2.2. Ammonium phosphate. (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub> – impregnation:** The following procedure was applied: 0.5 g of sample was added to 5 cm<sup>3</sup> 0.1 M H<sub>3</sub>PO<sub>4</sub> solution and mixed (magnetic stirrer). The pH of mixture was monitored by a pH-meter calibrated for two calibration points (pH = 1 and pH = 7). The mixture was neutralised (to pH = 7) by addition (dropwise) of 0.1 M solution of ammonium hydroxide NH<sub>4</sub>OH. The mixture was mixed for further 5 min and then oven dried at 333 K to constant weight. *Please note:* (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub> impregnated samples in text are called ‘neutralised’ samples.

### 2.3. Thermogravimetric analysis (TGA)

Pyrolysis tests were performed using a TGA analyser (Station Redcroft Simultaneous Analyser STA-780 Series). A typical sample mass of 10 mg was heated at 25 K/min in a purge of nitrogen with the final temperature of 1173 K, and then the sample was held at 1173 K for 15 min.

### 2.4. Analytical pyrolysis tests (PY–GC–MS)

Pyrolysis–gas chromatography–mass spectrometry (PY–GC–MS) tests were performed on each sample using a CDS 1000 pyrolyser coupled to an Agilent 5975 Series GC–MSD gas chromatograph. The column was a RTX 1701 (14% cyanopropyl-phenyl, 86% dimethylpolysiloxane; 60 m, 0.25 mm i.d., 0.25 μm d.f.). The gas chromatograph oven was held at 313 K for 2 min and then programmed at 4 K/min to 523 K, held for 30 min. Approximately 2 mg of sample was placed in 20 mm quartz tube in between quartz wool. The sample was pyrolysed at a set point temperature of 873 K at a ramp rate of 20 K/ms with the final dwell time of 20 s.

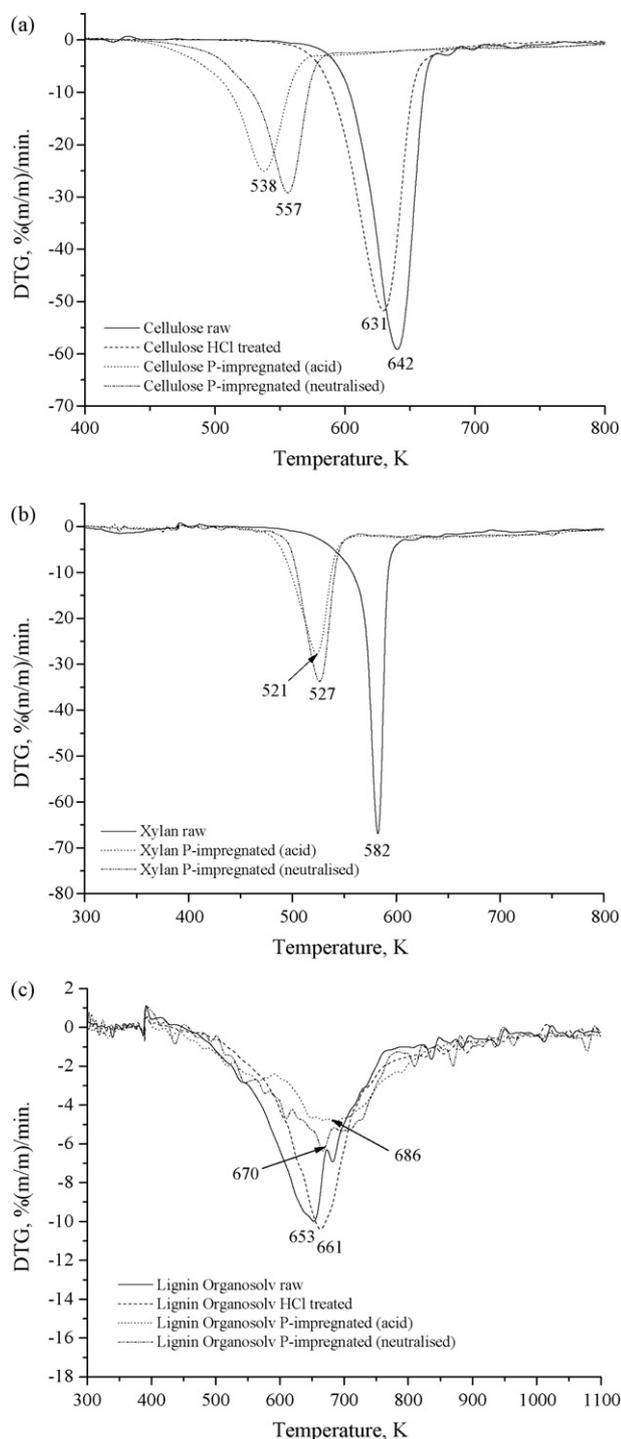
## 3. Results and discussion

### 3.1. Biomass components (model compounds study)

#### 3.1.1. TGA pyrolysis

The differential thermogravimetric (DTG) results comparing the impact of phosphorus in the TGA pyrolysis experiments of cellulose, xylan and Organosolv lignin are shown in Fig. 1. Pyrolysis yields from these studies are given in Table 1.

The decomposition of untreated cellulose (Fig. 1a) occurs in the temperature region between 448 K and 676 K, with the maximum peak temperature at 642 K. Demineralisation shifts the maximum peak temperature to 631 K, within the same temperature region. As discussed previously [2], this is thought to be due either to the removal of catalytic metals through demineralisation, or due to a modification (lowering) of the average cellulose MW by the acid treatment. Phosphorus addition significantly changes the



**Fig. 1.** Differential thermogravimetric analysis (DTG) for the pyrolysis of differently treated (a) cellulose, (b) xylan and (c) lignin.

decomposition profile. The acid impregnated cellulose sample decomposes between 445 K and 572 K, with the maximum peak temperature at 538 K. Ammonium phosphate impregnated cellulose (neutralised sample) has a very similar profile and starts to decompose at 453 K with the peak temperature at 557 K; the decomposition process is finished by 583 K. In both cases, single-step decomposition processes are observed. The addition of phosphorus to cellulose also has a dramatic influence on the pyrolysis product distribution—significant increases in yields of char are noted, from 6.9% for the demineralised sample to 22.4%

**Table 1**  
Pyrolysis yields from TGA studies of treated model compounds

Sample	Pyrolysis yields (%)	
	Volatiles	Char
Cellulose raw	92.9	7.1
Cellulose HCl treated	93.1	6.9
Cellulose P-impregnated (acid)	77.6	22.4
Cellulose P-impregnated (neutralised)	69.6	30.4
Xylan raw	76.9	23.1
Xylan P-impregnated (acid)	66.2	33.8
Xylan P-impregnated (neutralised)	68.7	31.3
Lignin Organosolv raw	60.5	39.5
Lignin Organosolv HCl treated	59.1	40.9
Lignin Organosolv P-impregnated (acid)	51.7	48.3
Lignin Organosolv P-impregnated (neutralised)	53.1	46.9

and 30.4% for acid and neutralised sample, respectively. Increasing char yield is thought to be the result of acid catalysed condensation reactions [11].

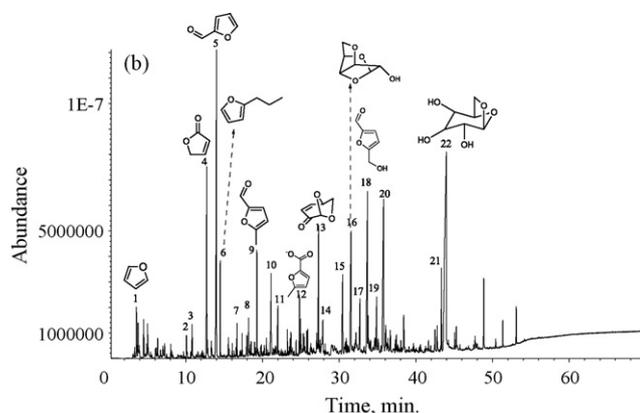
The DTG profile for xylan pyrolysis is shown in Fig. 1b. The DTG curve for the unimpregnated sample showed the peak maximum at 582 K. The presence of phosphorus shifts the maximum peak temperature downwards (by approximately 60 K) to 521 K for the acid impregnated sample and 527 K for the neutralised sample. The shape of DTG curve for raw xylan indicates that the decomposition, once initiated, occurs more rapidly than for the phosphorus impregnated samples. Phosphorus also increases the char yield of xylan from 23.1% to 33.8% for the acid impregnated sample and from 23.1% to 31.3% for the neutralised sample (Table 1). We can speculate that both the catalytic action and the increased char yields are brought about in an analogous way to the cellulose sample, i.e. phosphorus salts catalyse dehydration reactions of xylans.

As shown in Fig. 1c the major mass loss for all lignin samples occurs between 480 K and 800 K, giving broad peaks with the maximum temperatures at 653 K and 661 K for raw and demineralised sample, respectively. When phosphorus is added to the lignin samples the maximum peak temperature of catalysed pyrolysis is shifted slightly to higher temperature. Peak temperatures were observed at 686 K and 670 K for phosphoric acid impregnated lignin and  $(\text{NH}_4)_3\text{PO}_4$  impregnated (neutralised) lignin, respectively. The demineralisation process has no influence on char yield, but for phosphorus impregnated samples the char yields are increased by approximately 6–7% to values of 48.3% and 46.9 for acid and neutralised samples, respectively (Table 1).

### 3.1.2. PY-GC-MS studies

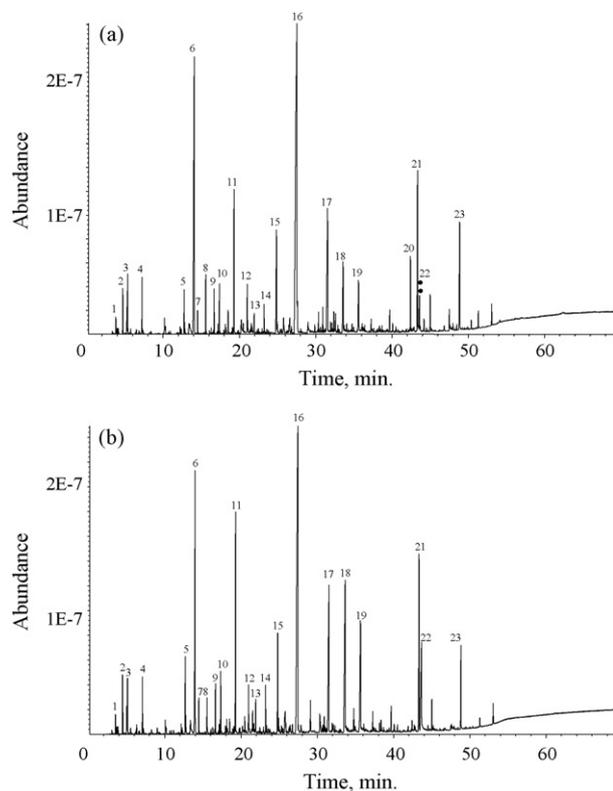
Pyrolysis–gas chromatography–mass spectrometry (PY-GC-MS) analysis has been introduced to study the generation of light and medium volatile organics formed during pyrolysis. Assignments of the main peaks were made from mass spectral detection (NIST05a MS library) and from the literature [16–18] and are given under the each figure. Thus, the assignments given in this paper are likely assignments based on mass spectra and previous work, but have not been definitively elucidated. Chromatograms from PY-GC-MS analyses of raw and demineralised cellulose were very similar, and the trace for the latter is given in Fig. 2. Fig. 3 displays the acid and neutralised phosphorus impregnated cellulose samples. Selected cellulose key markers were identified for the most abundant thermal degradation compounds, and their structural formulas are added to Fig. 2.

The main cellulose thermal degradation products for the uncatalysed pyrolysis have been analysed previously [19] and, comprise: 2(5H)-furanone; furfural; 5-methyl-2-furancarboxaldehyde; 5-hydroxymethyl-2-furancarboxaldehyde; Sugars



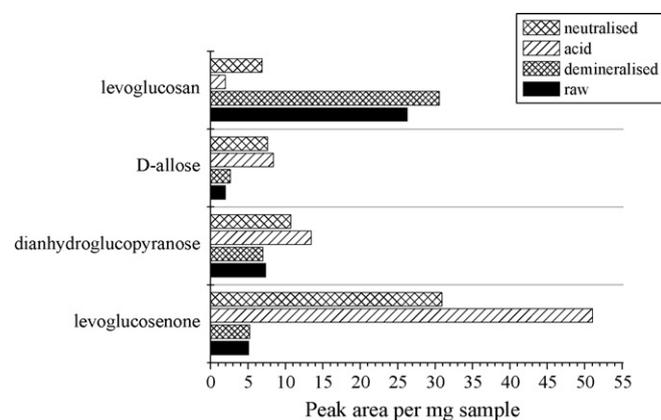
**Fig. 2.** Pyrolysis–GC–MS of demineralised cellulose.

The main peaks are assigned from mass spectral detection as follows: 1: furan; 2: 3-methyl-furan; 3: 2-propenoic acid, methyl ester; 4: 2(5H)furanone; 5: furfural; 6: 2-propyl-furan; 7: 1-(2-furanyl)-ethanone; 8: 1,2-cyclopentanedione; 9: 5-methyl-2-furancarboxaldehyde; 10: 3-methyl-1,2-cyclopentanedione; 11: 2,4-dihydroxy-6-methyl-2H-pyran-2-one; 12: 3-furan-carboxylic acid, methylester; 13: levoglucosenone; 14: 3,5-dihydroxy-2-methyl-4H-pyran-4-one; 15: 3-methyl-1,2-cyclopentenediol; 16: 1,4:3,6-dianhydro-α-D-glucopyranose; 17: Unknown; 18: 5-hydroxymethyl-2-furancarboxaldehyde; 19: 1,2-cyclohexanedione; 20: Not confirmed; 21: D-allose; 22: levoglucosan.



**Fig. 3.** Pyrolysis–GC–MS of (a)  $H_3PO_4$  and (b)  $(NH_4)_3PO_4$  impregnated cellulose.

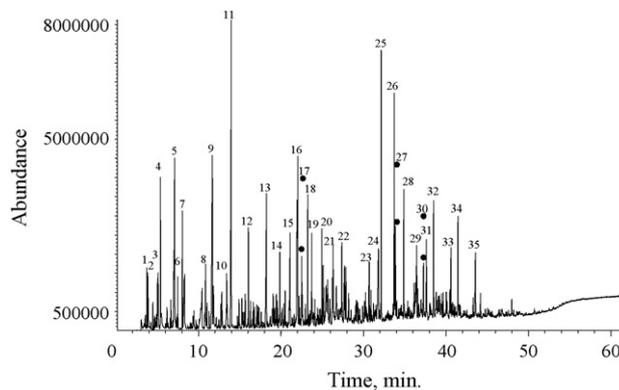
The main peaks are assigned from mass spectral detection as follows: 1: furan; 2: 2-methyl-furan; 3: 2-butanone; 4: acetic acid; 5: 2(5H) furanone; 6: furfural; 7: 2-propylfuran; 8: 5-methyl-2(3H) furanone; 9: 1-(2-furanyl)-ethanone; 10: 2-cyclopenten-1,4-dione; 11: 5-methyl-2-furancarboxaldehyde; 12: 5-methyl-2(5H)furanone; 13: 3-methyl-1,2-cyclopentanedione; 14: phenol; 15: 3-furan-carboxylic acid, methylester; 16: levoglucosenone; 17: 1,4:3,6-dianhydro-α-D-glucopyranose; 18: 5-hydroxymethyl-2-furancarboxaldehyde; 19: 4-O-b-D-galactopyranosyl-α-D-glucopyranose; 20: Unknown; 21: D-allose; 22: levoglucosan; 23: Unknown.



**Fig. 4.** Peak areas for key sugars from PY–GC–MS analysis of cellulose samples. (Peak areas have been normalised per mg of volatile products.)

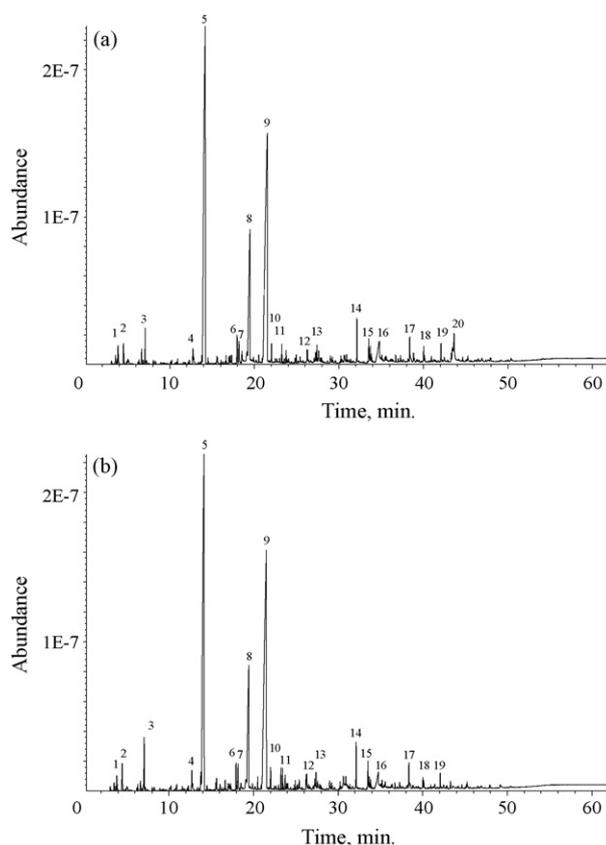
derivatives: (i) 1,6-anhydro-3,4-dideoxy- $\Delta^3$ - $\beta$ -D-pyranosen-2-one (levoglucosenone); (ii) 1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose; (iii) 4-O- $\beta$ -D-galactopyranosyl- $\alpha$ -D-glucopyranose; (iv) D-allose and (v) 1,6-anhydro- $\beta$ -D-glucopyranose (levoglucosan). Levoglucosan is reported as the major pyrolysis product of cellulose and is formed under neutral [20] or acid [21] conditions and it is generally accepted that generation of this anhydrosugar is the first step of the formation of other volatile compounds. This work has identified the other sugar derivatives listed above in addition to levoglucosan, although it is unclear if they are parallel (alternative) reaction products, or rearrangement from levoglucosan.

The presence of phosphorus changes decomposition profile. The major volatile products are: furfural; 5-methyl-2-furancarboxaldehyde, levoglucosenone, 1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose; 5-hydroxymethyl-2-furancarboxaldehyde and D-allose. Levoglucosan is still produced in similar yield, but it is no longer the major component. No large differences between the profiles (i.e. peak intensity/abundance) of acid and neutralised P-impregnated cellulose sample were observed.



**Fig. 5.** Pyrolysis–GC–MS chromatogram for raw xylan.

The main peaks are assigned from mass spectral detection as follows: 1: 3-methyl-1,2-cyclopentanedione; 2: acetone; 3: acetic acid; 4: propanoic acid; 5: acetic acid anhydride with formic acid; 6: 2,3-pentanedione; 7: 2,3-dihydro-1,4-dioxin; 8: 3-methyl butanal; 9: 1-hydroxy-2-butanone; 10: butanediol; 11: furfural; 12: 2-methyl-2-cyclopenten-1-one; 13: 1,2-cyclopentanedione; 14: 3-methyl-2-cyclopenten-1-one; 15: Unknown; 16: 3-methyl-1,2-cyclopentanedione; 17: 1,4-dimethyl-1,3-cyclopentanedione; 18: phenol; 19: 2-methoxyphenol; 20: 2,3-dihydroxybenzaldehyde; 21: 3-methylphenol; 22: 2,5-dimethyl phenol; 23: cyclohexane; 24: sucrose; 25: 2-methoxy-4-vinyl phenol; 26: 1,2-benzenediol; 27: 2,6-dimethoxy phenol; 28: 3-methyl-1,2-benzenediol; 29: D-mannose; 30: hydroquinone; 31: 3 hydroxybenzaldehyde; 32: 2-methyl-1,4-benzenediol; 33: 3',5'-dimethoxyacetophenone; 34: 3,4-dihydro-6-hydroxy-2H-1-benzopyran; 35: 2,6-dimethoxy-4-(2-propenyl)-phenol.



**Fig. 6.** Pyrolysis–GC–MS of (a)  $\text{H}_3\text{PO}_4$  and (b)  $(\text{NH}_4)_3\text{PO}_4$  impregnated xylan samples.

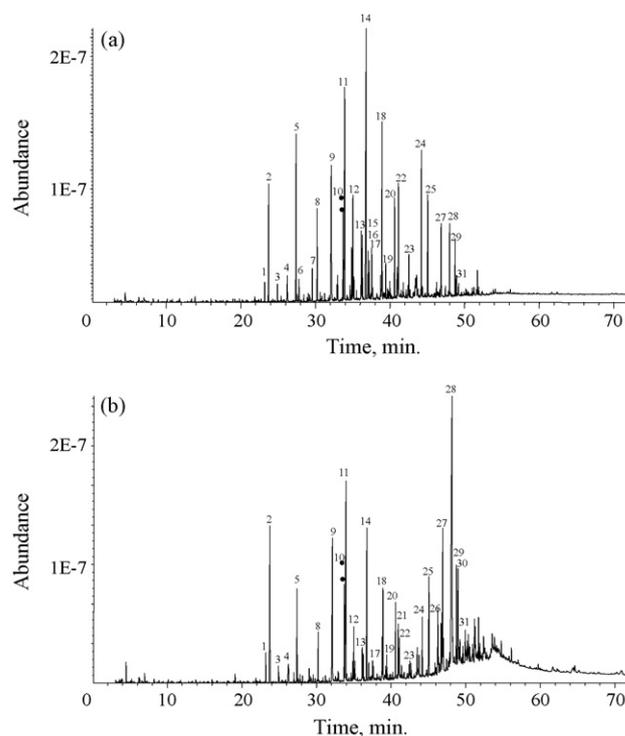
The main peaks are assigned from mass spectral detection as follows: 1: acetone; 2: 2-methyl-furan; 3: acetic acid; 4: 2,3-pentanedione; 5: furfural; 6: 1,2-cyclopentanedione; 7: 5-methyl-2-3H-furanone; 8: 3-methyl-2-cyclopenten-1-one; 9: 3,4-dihydro-2-methoxy-2H-pyran (or) 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one; 10: 3-methyl-1,2-cyclopentanedione; 11: 2-methoxyphenol; 12: 3-methylphenol; 13: 2,5-dimethyl phenol; 14: 12-methoxy-4-vinyl phenol; 15: 1,2-benzenediol; 16: 3-methyl-1,2-benzenediol; 17: 3-hydroxybenzaldehyde; 18: 1-(3-hydroxyphenyl)-ethanone; 19: 3,4-dihydro-6-hydroxy-2H-1-benzopyran; 20: 2,6-dimethoxy-4-(2-propenyl)-phenol.

Peak area percentages for sugar derivatives from the chromatograms in Figs. 2 and 3 were normalised per mg of volatile products. In this way peak areas for key sugar derivatives from the PY–GC–MS profiles could be compared in terms of the catalytic impact of phosphorus. This comparison is given in Fig. 4. (Furfural, a sugar decomposition product, is a major component in phosphorus-catalysed samples but not included in Fig. 4.) In both cases ( $\text{H}_3\text{PO}_4$  and  $(\text{NH}_4)_3\text{PO}_4$  impregnation), there is a significant influence of phosphorus on the formation of levoglucosenone and furfural and these are the main components. It is worth noting that the peak area percentages for the levoglucosenone were increased from the value of 5.2% to 51.0% (acid impregnation) and 30.9% (ammonium phosphate impregnation). This indicates strong catalytic impact of phosphorus on cellulose decomposition, favouring levoglucosenone formation as reported previously by Dobelet et al. [12] and Di Blasi et al. [10]. For our sample and conditions we see levoglucosenone:levoglucosan ratios to increase markedly upon addition of phosphorus, and this ratio is higher for the acid impregnated sample, compared to the ammonium phosphate impregnated sample. The highest levoglucosan yield for the demineralised cellulose sample, as the major 1,6-anhydrosaccharide product for the uncatalysed reaction [22].

Chromatograms from PY–GC–MS analyses of xylan as well as acid and neutralised P-impregnated xylan samples are given in

Figs. 5 and 6, respectively. The main decomposition products of the raw xylan sample are: propanoic acid; 1-hydroxy-2-butanone; furfural; 3-methyl-1,2-cyclopentanedione; 2-methoxy-4-vinyl phenol; 1,2-benzenediol and 2-methyl-1,4-benzenediol. The influence of added phosphorus on the nature of the xylan decomposition products is high, and produces a very noticeable change in the product distribution. Main degradation products are furfural (peak 5, retention time 14.2 min) and 3-methyl-2-cyclopenten-1-one (peak 8, retention time 19.8 min). A third main decomposition product (peak 9, retention time 21.1 min) is tentatively assigned 3,4-dihydro-2-methoxy-2H-pyran with  $m/z$  114 (parent ion?) and a strong fragmentation signal at  $m/z$  58; or 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one as cited by Fahmi et al. during pyrolysis of *Lolium* and *Festuca* grasses [23]. However, the NIST05a library probability match was low, suggesting co-elution. This simplified product distribution was present for both acid and neutralised phosphorus impregnated xylan.

The chromatograms for the HCl treated lignin (Organosolv) and  $\text{H}_3\text{PO}_4$  impregnated lignin are shown in Fig. 7. No difference between the product distributions from raw and HCl treated lignin samples as well as between  $\text{H}_3\text{PO}_4$  and  $(\text{NH}_4)_3\text{PO}_4$  impregnated samples were observed. Thus, the comparison has been made between the HCl treated sample and the  $\text{H}_3\text{PO}_4$  impregnated samples. Although the relative amounts change, the main



**Fig. 7.** Pyrolysis–GC–MS of (a) demineralised and (b)  $\text{H}_3\text{PO}_4$  impregnated Organosolv lignin.

The main peaks are assigned from mass spectral detection as follows: 1: phenol; 2: 2-methoxy-phenol; 3: 2-methyl-phenol; 4: 2-methoxy-3-methyl-phenol; 5: 2-methoxy-4-methyl-phenol; 6: 3,5-dimethyl phenol; 7: 4-ethyl-phenol; 8: 4-ethyl-2-methoxyphenol; 9: 3-methoxy-1,2-benzenediol; 10: 1,2-benzenediol; 11: 2,6-dimethoxyphenol; 12: 3,4-dimethoxy-phenol; 13: 2-methoxy-4-(1-propyl)-phenol; 14: 1,2,4-triethoxybenzene; 15: vanillin; 16: 2,5-diethyl-hydroquinone; 17: 1-(2,3,4-trihydroxymethyl)-ethanone; 18: 1,2,3-trimethoxy-5-methyl benzene; 19: 1-(4-hydroxy-3-methoxyphenyl)-ethanone; 20: 2-methoxy-4-(methoxymethyl)-phenol; 21: 1-ethyl-3-(phenylmethyl)-benzene; 22: 3-(4-hydroxy-3-methoxyphenyl)-2-propenoic acid; 23: 4-hydroxy-3-methoxy benzenoacetic acid; 24: 2,6-dimethoxy-4-(2-propenyl)-phenol; 25: 4-hydroxy-3,5-dimethoxy benzaldehyde; 26: 3,5-dimethoxy-4-hydroxyphenylacetic acid; 27: 1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone; 28: desaspidinol; 29: 1,2-dimethoxy-4-(1,2,3-methoxypropyl) benzene; 30: 3',5'-dimethoxyacetophenone; 31: aspidinol.

decomposition products of demineralised and both acid and neutralised lignin are: 2-methoxy-phenol; 2-methoxy-4-methyl-phenol; 3-methoxy-1,2-benzenediol; 2,6-dimethoxy-pheno; 1,2,4-trimethoxy-benzene; 1,2,3-trimethoxy-5-methyl-benzene; 2,6-dimethoxy-4-(2-propenyl)-phenol; 1,2-dimethoxy-4-(1,2,3-methoxypropyl)-benzene, desaspidinol and aspidinol. However, the presence of phosphorus during the pyrolytic decomposition of the lignin matrix decreases the abundance of 1,2,4-trimethoxy-benzene; 2-methoxy-4-methyl-phenol and 1,2,3-trimethoxy-5-methyl-benzene. Vanillin and 2,5-diethyl-hydroquinone were only detected in the raw and demineralised samples, while phosphorus catalysis promotes the generation of 1-(4-hydroxy-3-methoxyphenyl)-ethanone; 3,5-dimethoxy-4-hydroxyphenylacetic acid and 3',5'-dimethoxyacetophenone (not present in raw and HCl treated lignin samples). Phosphorus also significantly increased the abundance of desaspidinol and 1,2-dimethoxy-4-(1,2,3-methoxypropyl)-benzene. Also the larger amount of unresolved material eluting after 46 min is observed.

### 3.2. *Miscanthus × giganteus*

#### 3.2.1. TGA pyrolysis

Differential thermogravimetric results comparing the influence of phosphorus on the pyrolysis of the *Miscanthus × giganteus* biomass samples are shown in Fig. 8. The cell wall components of *Miscanthus* are 51.26% cellulose, 26.29% hemicellulose, 17.34% lignin. Raw *Miscanthus* has two main unresolved peaks. The first step of thermal degradation is attributed to the decomposition of hemicellulose and the initial stage of the degradation of cellulose, while the second step is attributed to the degradation of lignin and the final degradation of cellulose. Comparison with the cell wall components studied individually in Fig. 1, indicates that there is good agreement between peak maximum temperatures (582 K vs. 596 K for the hemicellulose decomposition peak, and 642 K vs. 649 K for the cellulose decomposition peak). Upon acid treatment to remove inorganic constituents from the biomass the first peak becomes much weaker indicating some change in the hemicellulose content. Also, the second main peak shifts to slightly higher temperature (peak temperature 654 K), which shows that some catalytic species have been removed by acid washing. In agreement with the work presented on the cell wall components in Fig. 1, upon addition of phosphorus, a strong catalytic effect on the degradation is observed. Peak maxima are shifted towards lower values: 546 K for acid impregnated *Miscanthus* and 554 K for neutralised

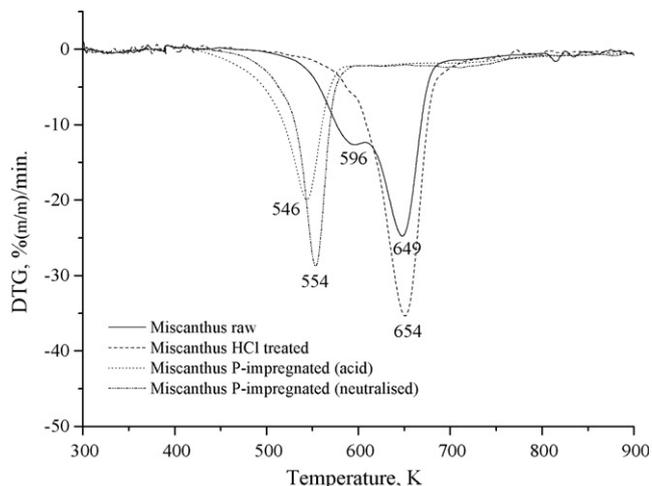


Fig. 8. DTG profiles for the pyrolysis of differently treated *Miscanthus × giganteus*.

Table 2

Pyrolysis yields from TGA studies of treated *Miscanthus* samples

Sample	Pyrolysis yields (%)	
	Volatiles	Char
<i>Miscanthus</i> raw	81.9	18.1
<i>Miscanthus</i> HCl treated	90.4	9.6
<i>Miscanthus</i> P-impregnated (acid)	68.1	31.9
<i>Miscanthus</i> P-impregnated (neutralised)	71.5	28.5

sample (cf. 538 K and 557 K for acid and neutralised P-impregnated cellulose, respectively).

The yields for TGA pyrolysis of *Miscanthus* samples are given in Table 2. HCl treatment decreases the char yield (from 18.1% for raw *Miscanthus* to 9.6% for the demineralised one), presumably because inorganic constituents that promote char formation are no longer present, a similar finding has been observed for willow [2]. The presence of phosphorus is again seen to have a large influence on the char formation stage, increasing the char yield, and this is more significant in the acid impregnated sample. Thus, it appears that phosphorus introduced as  $H_3PO_4$  is more effective in catalysing pyrolysis in the *Miscanthus × giganteus*, as seen by a larger decrease in the peak maximum temperature in the DTG plot (Fig. 8), and a larger increase the char yield (Table 2).

#### 3.2.2. PY-GC-MS studies

Chromatograms from PY-GC-MS analyses demineralised *Miscanthus* as well as acid and neutralised P-impregnated samples are given in Figs. 9–11, respectively. There are some similarities between the raw and demineralised *Miscanthus × giganteus* samples and only the latter is given in Fig. 9. The same cellulose and lignin key markers were detected in pyrolysis products of both samples. Peaks are identified for: cyclopentane derivatives (i.e. 1,2-cyclopentanedione, 3-methyl-1,2-cyclopentanedione); 2(5H)-furan; furfural; phenol and phenol derivatives (i.e. 2-methoxy-phenol, 3- and 4-methyl-phenol, 4-ethyl-phenol, 2-methoxy-4-methyl-phenol, 2,6-dimethoxyphenol; 2-methoxy-4-(2-propenyl)phenol); 1,2,4-trimethoxybenzene; 3',5'-dimethoxyacetophenone; 1,2-benzenedimethanol.

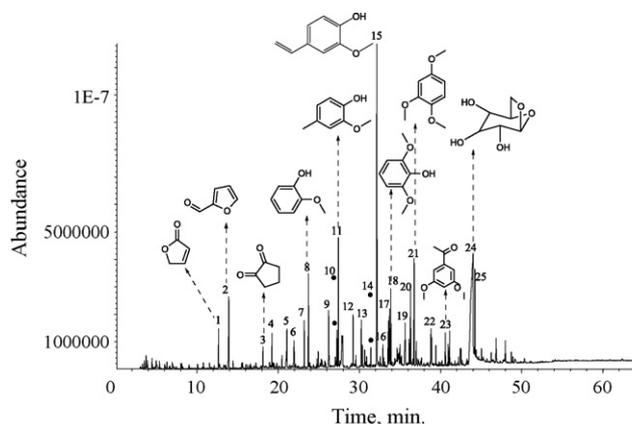
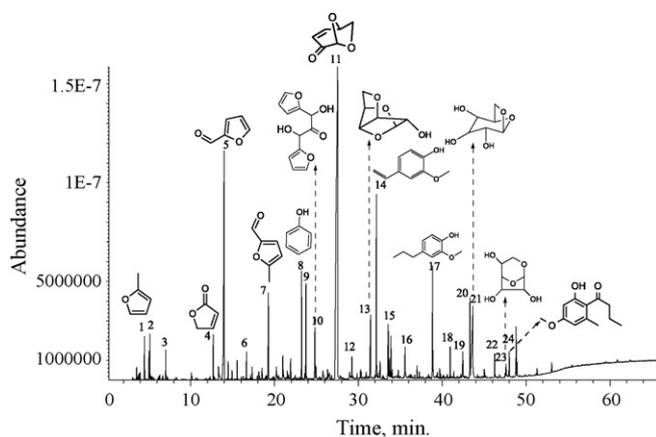


Fig. 9. Pyrolysis-GC-MS of demineralised *Miscanthus*.

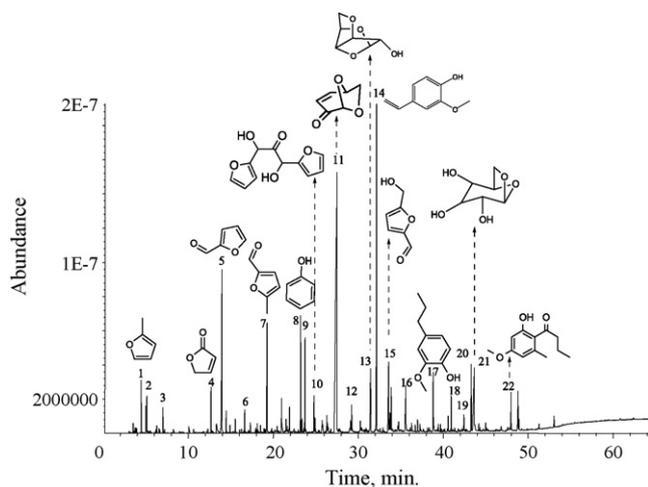
The main peaks are assigned from mass spectral detection as follows: 1: 2(5H)-furanone; 2: furfural; 3: 1,2-cyclopentanedione; 4: 5-methyl-2-furancarboxaldehyde; 5: 3-methyl-1,2-cyclopentanedione; 6: 2-methyl-1,2-cyclopentanedione; 7: phenol; 8: 2-methoxy-phenol; 9: 3- or/and 4-methyl-phenol; 10: levoglucosenone; 11: 2-methoxy-4-methyl-phenol; 12: 4-ethyl-phenol; 13: 4-ethyl-2-methoxy-phenol; 14: 1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose; 15: 2-methoxy-4-vinyl-phenol; 16: eugenol; 17: 1,2-benzenediol; 18: 2,6-dimethoxyphenol; 19: 4-methyl-1,2-benzenediol; 20: 2-methoxy-4-(1-propenyl)phenol; 21: 1,2,4-trimethoxybenzene; 22: 2-methoxy-4-propylphenol; 23: 3',5'-dimethoxyacetophenone; 24: levoglucosan; 25: 2-methoxy-4-(2-propenyl)phenol.



**Fig. 10.** Pyrolysis–GC–MS for acid P-impregnated Miscanthus.

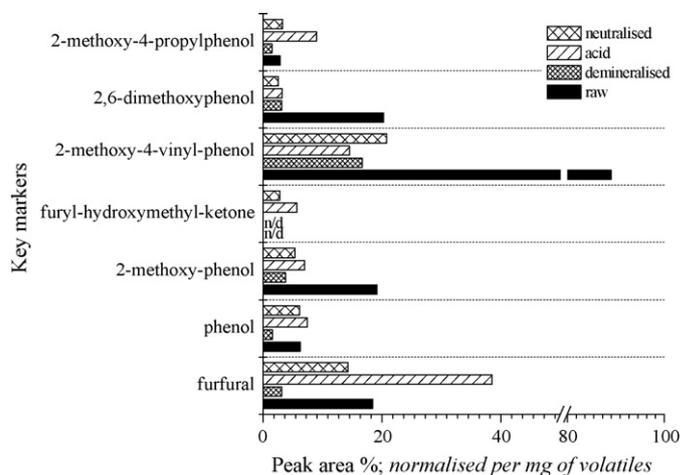
The main peaks are assigned from mass spectral detection as follows: 1: 2-methylfuran; 2: 2-butanone; 3: acetic acid; 4: 2(5H)furanone; 5: furfural; 6: 1-(2-furanyl)-ethanone; 7: 5-methyl-2-furancarboxaldehyde; 8: phenol; 9: 2-methoxyphenol; 10: furyl-hydroxymethyl ketone; 11: levoglucosone; 12: 4-ethyl-phenol; 13: 1,4:3,6- dianhydro- $\alpha$ -D glucopyranose; 14: 2-methoxy-4 vinyl-phenol; 15: 5-hydroxymethyl- 2-furan-carboxaldehyde; 16: 4 methyl-1,2-benzenediol; 17: 2-methoxy-4- propylphenol; 18: 1-(4-hydroxy-3-methoxyphenyl)-2-propanone; 19: 2,4'-dihydroxy- 3'-methoxyacetophenone; 20: D-allose; 21: levoglucosan; 22: 3,5 dimethoxy-4- hydroxyphenylacetic acid; 23: 1,6-anhydro- $\alpha$ -D galactofuranose; 24: desaspidinol.

The main decomposition products of acid impregnated and neutralised Miscanthus samples (Figs. 10 and 11) are: 2(5H)-furan, furfural; 5-methyl-2-furancarboxaldehyde, phenol and phenol derivatives (2-methoxy-phenol; 4-ethyl-phenol; 2-methoxy-4-propylphenol); 2-methoxy-4-vinyl-phenol and sugars (dianhydroglucopyranose and levoglucosan). Levoglucosone is seen as an intense peak, which agrees with the findings from the studies of P-impregnated cellulose (see Fig. 3). Furfural is also detected as a high intensity product from pyrolysis of the P-impregnated Miscanthus, and this was duplicated in pyrolysis



**Fig. 11.** Pyrolysis–GC–MS for neutralised P-impregnated Miscanthus.

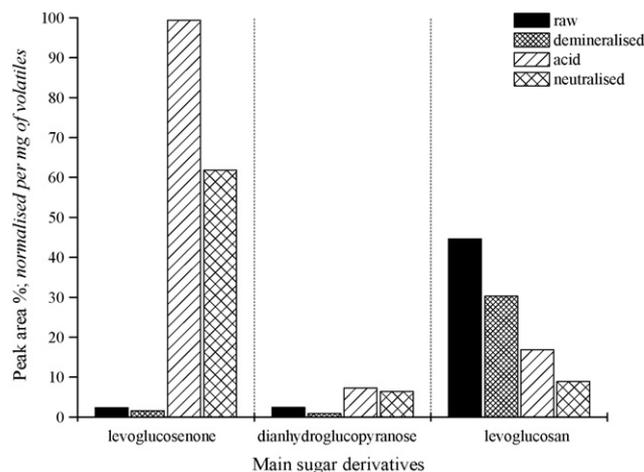
The main peaks are assigned from mass spectral detection as follows: 1: 2-methylfuran; 2: 2-butanone; 3: acetic acid; 4: 2(5H)furanone; 5: furfural; 6: 1-(2-furanyl)-ethanone; 7: 5-methyl-2-furancarboxaldehyde; 8: phenol; 9: 2-methoxyphenol; 10: furyl-hydroxymethyl ketone; 11: levoglucosone; 12: 4-ethyl-phenol; 13: 1,4:3,6-dianhydro- $\alpha$ -D glucopyranose; 14: 2-methoxy-4 vinyl-phenol; 15: 5-hydroxymethyl-2-furan-carboxaldehyde; 16: 4-methyl 1,2-benzenediol; 17: 2-methoxy-4- propylphenol; 18: 1-(4-hydroxy-3 methoxyphenyl)-2-propanone; 19: 2,4'-dihydroxy- 3' methoxyacetophenone; 20: D-allose; 21: levoglucosan; 22: desaspidinol.



**Fig. 12.** Peak areas for key cellulose and lignin markers from PY–GC–MS analysis for Miscanthus samples (all treatments). (Peak areas have been normalised per mg of volatile products.)

studies of both cellulose and xylan (Figs. 3 and 6). However, one of the major products from P-impregnated xylan (peak 9, Fig. 6) is not evident in high concentrations in the P-impregnated Miscanthus (Fig. 9), even though Miscanthus contains 26% hemicelluloses. However, there may be branching and cross-linking differences in the individual hemicellulose contents of Miscanthus compared to oat spelt xylan, which would impact on the nature of the pyrolysis fragments.

Some peak area percentages from the chromatograms in Figs. 9–11 were normalised per mg of volatile products and compared in Fig. 12. The peak areas for the three sugar derivatives (levoglucosone, 1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose and levoglucosan) are compared in Fig. 13. It is clear that phosphorus has a significant influence on the formation of volatile products. Acid (phosphorus) treatment promotes decomposition of levoglucosan and significantly increased the yield of levoglucosone and 1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose at the expense of levoglucosan. The amount of the furfural in the tars also increases. Demineralisation lowers yields of methoxyl phenols and 2-methoxy-4-vinyl-phenol. The latter is one of the major of the products from raw Miscanthus and presumably arises from xylan decomposition (cf. Fig. 5), since demineralisation removes some of the hemicellulose component.



**Fig. 13.** Peak areas for key sugar derivatives from PY–GC–MS analysis for Miscanthus samples (all treatments). (Peak areas have been normalised per mg of volatile products.)

#### 4. Conclusions

The main cell wall constituents (cellulose, xylan, lignin) as well as *Miscanthus × giganteus* sample were subjected to three types of pre-treatment – HCl demineralisation and impregnation of the demineralised samples by ortho-phosphoric acid – H<sub>3</sub>PO<sub>4</sub> – and ammonium phosphate – (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>.

In this study it was observed that the phosphorus salts catalysed the pyrolysis and that the yields of pyrolysis products were modified. The phosphorus-catalysed pyrolytic decomposition resulted in a large increase in char yield for all samples, but particularly for cellulose and *Miscanthus*. For example the char yield increased from 6.9% for demineralised cellulose to 22.4% and 30.4% for the acid impregnated and neutralised samples. Also in the case of *Miscanthus* sample char yield is seen to triple. DTG analysis revealed that the thermal degradation processes of cellulose, xylan and *Miscanthus* samples occur in one step and the main pyrolysis step is shifted to lower temperature by approximately 100 K. A small impact of phosphorus was observed in the case of lignin pyrolysis char yields and types of pyrolysis decomposition products produced.

The tar components produced from phosphorus impregnated and demineralised samples were very different. Levoglucosan is a major component produced in fast pyrolysis of cellulose. Furfural and levoglucosenone become more dominant products upon P-impregnation pointing to new rearrangement and dehydration routes. This is true regardless of whether phosphorus is added as phosphoric acid or ammonium phosphate.

The P-catalysed xylan decomposition route leads to a much smaller mixture of products, which are dominated by furfural, 3-methyl-2-cyclopenten-1-one and one other product, possibly 3,4-dihydroxy-2-methoxy-2H-pyran or 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one.

Phosphorus-catalysed lignin decomposition route also leads to a modified mixture of tar components and desaspidinol as well as other higher molecular weight component become more dominant relative to the methoxyphenyl phenols, dimethoxy phenols and triethoxy benzene.

The results for *Miscanthus* corroborated the cell wall component work where, with one exception, similar products were identified. This again leads to the conclusion that the under-

standing of the fast pyrolysis of biomass can be gained through the study of the individual cell wall components, provided consideration is given to the presence of catalytic components such as phosphorus (and potassium).

The work gives mechanistic insight into P-catalysed pyrolysis and has implication in the production of useful chemicals and products from biomass pyrolysis.

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