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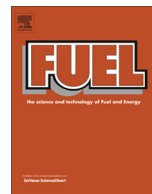
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Miscanthus combustion properties and variations with Miscanthus agronomy ☆

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HIGHLIGHTS

- We present findings from a two-year field trial into Miscanthus agronomy.
- We examine changes in fuel composition and characteristics.
- Agronomy influences fuel characteristics especially N, Cl, and ash.
- Agronomy indirectly influences combustion characteristics.

ARTICLE INFO

ABSTRACT

A study of the interaction of agronomy and its effects on fuel quality has been carried out for *Miscanthus x giganteus* grown in the UK through the UK's SUPERGEN Bioenergy Consortium activities. Work on Miscanthus yield responses to N, K and S fertilizer will be reported elsewhere, and this study is focused on how fertilisers affected Miscanthus fuel quality. Six different fertiliser treatments were chosen to give interesting contrasts from the field experiment investigating yield responses; nitrogen (ammonium nitrate) at 0, 100, 150 and 250 kg N ha^{-1} in combination with potassium (K as KCl) at 50 kg K ha^{-1} and 150 kg N ha^{-1} also with zero K, and with 50 kg K ha^{-1} (K as K_2SO_4). A total of 270 samples were taken at five time points over the autumn and winter harvest window in each of the two growth years, 2005 and 2006. Results show that Miscanthus stems have better fuel quality than leaves, with much lower ash, N and S contents, and slightly higher C concentrations and hence higher estimated calorific value. The treatment without any N added into fertiliser seems to give a better fuel quality than other treatments considered in the study, resulting in a fuel with lower N, ash content, and a lower propensity to fouling (as indicated by the indices calculated from its ash analysis), and also higher C concentrations. In general, the late harvested Miscanthus samples have better fuel quality, with lower N, Cl, ash contents, alkali index and slightly higher C contents.

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1. Introduction

The increasing demand for energy and the resulting environmental impact of fossil fuels have seen many turn to renewable energy sources as a sustainable, clean alternative. Energy crops, grown for the specific purpose of their energy value, could be sustainable and secure energy sources for power stations in the UK. The whole process of energy crop utilisation, including fuel supply, combustion systems, solid residue and gaseous emissions, are strongly influenced by the physical and chemical characteristics of the crop. Some of the most important physical properties of fuels include moisture content, bulk density, physical dimension and size distribution. Important chemical properties are elemental contents, such as carbon, hydrogen, nitrogen, chlorine, and sulphur, and also their content of volatiles, ash, and metals, which have an impact on any corrosion problems and/or the formation of deposits in the boiler. All these parameters need to be considered in the design of a combustion system and for this prior knowledge of the biomass characteristics is needed. Carbon, hydrogen and oxygen are the main elemental components of biomass fuels and their relative proportions affect the heating value (calorific value) of fuels. The carbon content in biomass is around 50% on a dry basis compared to coal, which is more than 80% [1,2]. Carbon in biomass fuels is present in partly oxidised forms, resulting in biomass containing higher oxygen and volatile matter contents than coal. The

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volatile content in biomass varies between 70% and 85% (dry basis), whereas in a typical bituminous coal, it is about 18% (dry basis) [2]. Although nitrogen oxide (NO_x) emissions are strongly influenced by the combustion system, the fuel bound N can be a significant source of NO_x during biomass combustion processes at temperatures between 800 and 1100 °C [2–4]. Depending on the fuel type, the operational temperature and the residence time, the nitrogen partitioning (i.e. the split of nitrogen between volatiles and char) is roughly proportional to the volatile matter in the fuel [5], and as such, typically 80–90% of the fuel-N is released with volatiles [6].

The Cl, S and metal contents of biomass fuels are responsible for ash related problems, such as slagging and fouling, corrosion and agglomeration. During combustion, the inorganics such as K, Ca, P, Fe, S and Cl, are partially volatilised and released into the vapour phase. At high temperatures and in the presence of SiO_2 or SiO, K can be absorbed by the silicates forming a low melting potassium silicate. During the cooling process, the gaseous potassium may condense on the coarse fly ash as potassium chloride (KCl) or potassium sulphate (K_2SO_4). This low melting point fly ash may stick or form a deposit on boiler tubes, creating a low-melting point sticky surface. Corrosion may occur on metallic tube surfaces as a result of the chlorine content in the depositions. So, these ash depositions can cause slagging, fouling, agglomeration and corrosion depending upon the deposition and transformation of the inorganic components found in the different region of the boiler. The degrees of fouling and slagging vary with fuel characteristics as well as the local gas temperatures, tube temperature and local heat flux on each particle [7]. Hence research into biomass fuel characterisations, ash deposition and prediction are vital for fuel utilisation, as they affect boiler performance and efficiency.

Certain metals in the fuel also influence the thermal decomposition, which is a very important step in biomass combustion. The rate of devolatilisation and its onset temperature, ignition and the composition of the volatiles influence boiler design, combustion processes and other thermal processing methods, such as fast pyrolysis [8–10]. A fuel with a lower volatile combustion peak temperature (temperature at which the maximum rate of devolatilisation occurs) is more reactive so less energy is needed for its pyrolysis. Previous work studying the combustion of Reed Canary Grass (*Phalaris arundinacea*) and switchgrass (*Panicum virgatum*) [11] has shown that the peak temperature for volatile combustion decreases as the K content of fuel increases. This is due to the catalytic impact of potassium, although its influence was less clear for char combustion [11]. The catalytic influence of other metals on the volatile combustion peak temperatures, such as Ca, Mg, Fe, and P has also been investigated [12]. However, K is the most problematic element in ash because of the associated slagging and fouling problems in boilers. A balance needs to be found, or both factors need to considered when choosing an optimum biomass fuel.

Previous work has looked at Miscanthus crop yield responses to fertiliser applications of nitrogen, potassium and sulphur [13]. The present study is focused on characterising and evaluating the quality of *Miscanthus x giganteus* as a fuel using series of techniques. The aim of the investigation is to reveal how crop agronomy affects fuel combustion properties; certain nutrients are vital for plants to carry out fundamental growth and reproduction, but risk being potentially detrimental to fuel combustion quality.

2. Experimental methods

2.1. Fuel samples

Miscanthus (*Miscanthus x giganteus*) was grown by Rothamsted Research at the Woburn Experimental Farm in the South East of the UK (52 01°N, 00 36°W, *ca.* 90 m AOD). The experimental design was a complete randomised block design with three replicates. The original experimental design incorporated 14 different agronomic treatments, where nitrogen in the form of ammonium nitrate and potassium in the form of KCl or K_2SO_4, were added to the field as fertilizers in varying quantities; between 0–250 kg of N per hectare and 0–100 kg of K per hectare. A subset of 6 treatments was selected for this study to encompass the effect of N rate and K form. The treatments chosen for this study and sampling dates are listed in Table 1. Treatments can be identified by N_nK_mC or $N_{n-}K_mS$, where *n* refers to the quantity of N-fertilizer added in units of 50 kg N, *m* refers to the quantity of K-fertilizer added in units of 50 kg K, and C and S refer to if the K fertilizer was KCl or K_2SO_4. The soil at the site was a sandy loam derived from Stackyard/Lowland Brown Sands over sandy colluviums or lower greensand [14]. The crop was planted in April 2003, in a plot size 10 × 12 m. The crops were sampled 5 times through the autumn and winter following the third (2005) and fourth (2006) growing season and corresponding to the harvest window for Miscanthus (see Table 1). At each sampling time, samples were cut from a randomly selected area of 1 m^2 in each plot. The leaves and stems were separated at early sampling dates to be able to study the different components of the crop. As the crop matured, very little leaf remained on the plant and the samples were treated more as a commercial harvest, where stem plus any remaining leaf is collected. Therefore, 45 samples were obtained for each treatment over a two year growing period; hence a total of 270 samples were studied for their combustion and ash characteristics. All samples were oven dried at 80 °C for 36 h, and then milled and sieved to less than 600 μm, prior to storage in plastic tubs and small gas-tight glass bottles. All the analyses were carried out from October 2007 to May 2008 for crop harvested in 2005/2006 (3rd year crop) and May 2008 to November 2009 for crop harvested in 2006/2007 (4th year crop).

2.2. Fuel analysis

The C, H, N content of the samples from treatments 1, 2 and 4 (3rd year crop) were analysed by the Chemistry department analytical services while the rest of the treatments were determined by the SPEME research laboratory, both at the University of Leeds. The samples were split between the departments due to equipment availability. Both departments determine CHN contents by flash combustion.

The calorific value or higher heating value (CV) of the samples were calculated using the method developed by Friedl et al. [15], where 122 biomass samples were selected to develop a regression model for predicting the higher heating value of a fuel from its elemental composition (dry basis %), as given by the following equation:

$$HHV = 3.55C^2 - 232C - 2230H + 51.2C \times H + 131N + 20,600 \qquad (E.1)$$

2.3. Ash analysis

The ash content of the samples were determined in accordance with the British Standard CEN/TS 14775:2004 [16]. The metal contents of the samples (Ca, Fe, K, Mg, Na, S and P) were analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP–OES). The chloride content was analysed by water extraction prior to analysis by continuous flow colorimetric analysis using a Skalar SAN^{PLUS} System. The silica contents were determined from the sample ash (as prepared by the British Standard) by spectrophotometry using a Jenway 6300 Spectrophotometer. More details of

Table 1
Sampling of Miscanthus crops: Fertiliser treatments applied and sampling dates.

Sampling time	Treatment 1 (N_0K_1C) 0 kg of N and 50 kg of KCl	Treatment 2 (N_2K_1C) 100 kg of N and 50 kg of KCl	Treatment 3 (N_3K_1C) 150 kg of N and 50 kg of KCl	Treatment 4 (N_5K_1C) 250 kg of N and 50 kg of KCl	Treatment 5 (N_3K_0) 150 kg of N and 0 kg of KCl	Treatment 6 (N_3K_1S) 150 kg of N and 50 kg of K_2SO_4
3rd year crop						
03/11/05	Leaf/stem	Leaf/stem	Leaf/stem	Leaf/stem	Leaf/stem	Leaf/stem
19/12/05	Leaf/stem	Leaf/stem	Leaf/stem	Leaf/stem	Leaf/stem	Leaf/stem
01/02/06	Leaf/stem	Leaf/stem	Leaf/stem	Leaf/stem	Leaf/stem	Leaf/stem
07/03/06	Whole crop	Whole crop	Whole crop	Whole crop	Whole crop	Whole crop
19/04/06	Whole crop	Whole crop	Whole crop	Whole crop	Whole crop	Whole crop
4th year crop						
25/09/06	Leaf/stem	Leaf/stem	Leaf/stem	Leaf/stem	Leaf/stem	Leaf/stem
07/11/06	Leaf/stem	Leaf/stem	Leaf/stem	Leaf/stem	Leaf/stem	Leaf/stem
08/01/07	Whole crop	Whole crop	Whole crop	Whole crop	Whole crop	Whole crop
26/02/07	Whole crop	Whole crop	Whole crop	Whole crop	Whole crop	Whole crop
26/03/07	Whole crop	Whole crop	Whole crop	Whole crop	Whole crop	Whole crop

the metal and silica analysis procedures can be found in Baxter et al. [17].

2.4. Burning profiles by thermogravimetric analysis (TGA)

Burning profiles of all samples were obtained using a Stanton Redcroft Simultaneous Analyser STA – 780 Series. For this purpose, 3.5–5 mg of sample were heated at a rate of 25 °C/min to a final temperature of 900 °C, under a constant flow of air at a rate of 50 ml/min.

2.5. Genstat statistical data analysis

The statistical software Genstat (GenStat® 2009 Twelfth Edition, VCN International Ltd.) was used to analyse the data. All the information presented here with respect to the Genstat software is
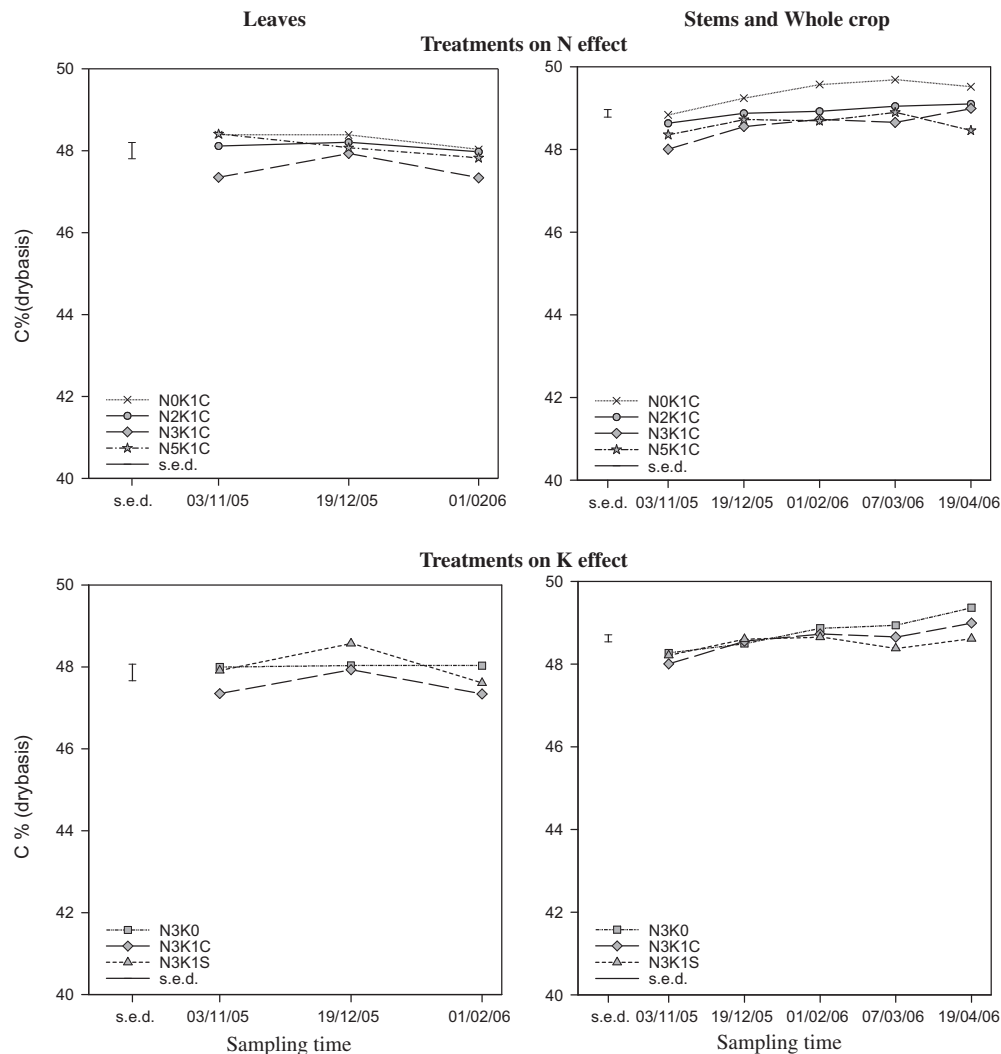

Fig. 1. Plot of the mean C (wt% db) contents for the different treatments over the sampling period (3rd year crop).
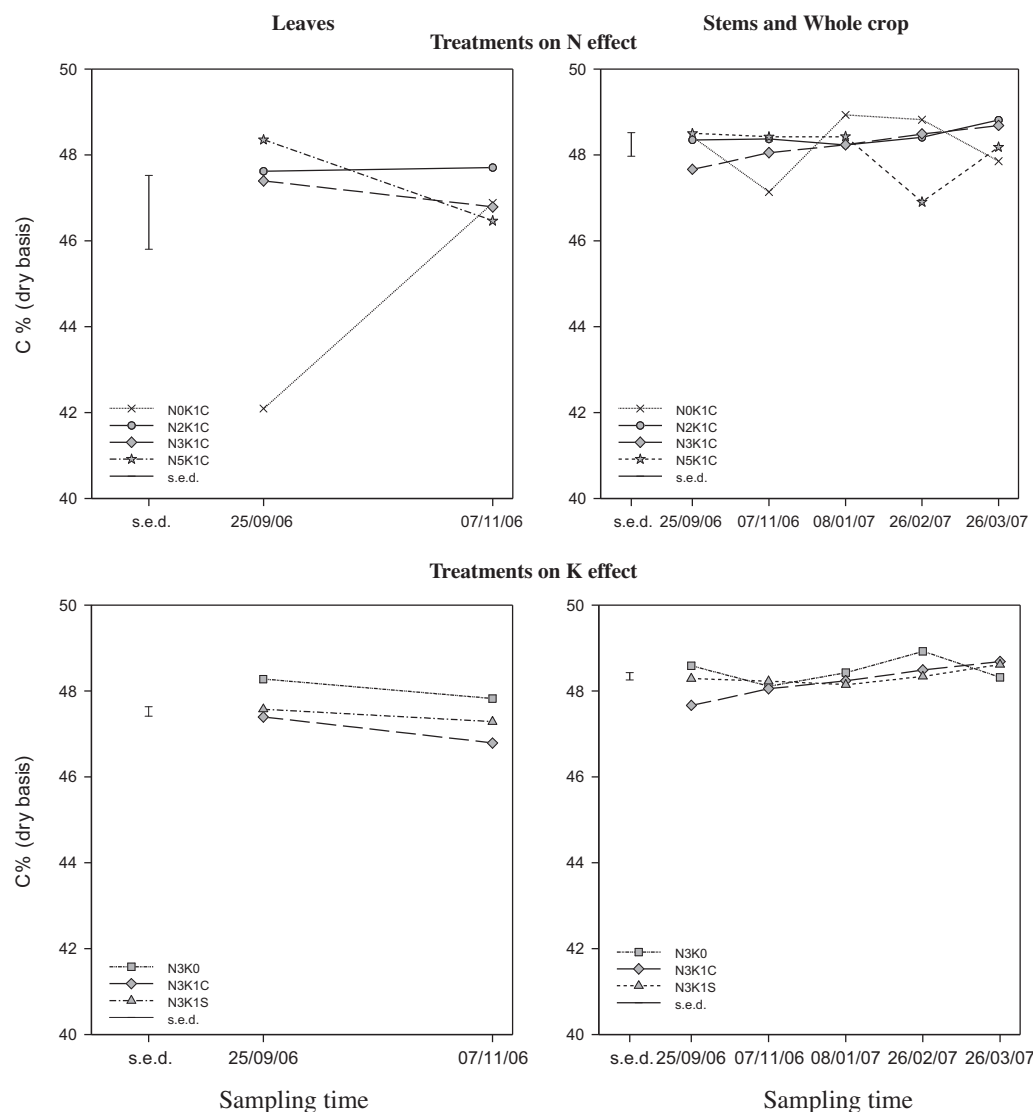
Fig. 2. Plot of the mean C (wt% db) contents of: (a) leaves and (b) stems and whole crops, for the different treatments over the sampling period (4th year crop).

based on Payne et al. [18]. Genstat provides a general framework for the testing of hypotheses and the estimation of treatment means and treatment comparison. In this study, comparisons of the Miscanthus treatments and their effect on the combustion properties of the resultant fuel were performed through Analysis of Variance (ANOVA) using the *repeat measurements* option. Although different samples were taken at each sampling time, they were from the same plot, therefore for the purpose of this study they were regarded as repeat measurements at each sampling time. The treatment comparisons were separated in two groups: one looks at the effect of the N fertiliser only, and the other at the effect of the K fertiliser only, on the fuel combustion properties. To study the effect of the N fertiliser, four treatments were considered (Table 1): treatment 1 (N_0K_1C, with 0 kg of N), treatment 2 (N_2K_1C, with 100 kg of N), treatment 3 (N_3K_1C, with 150 kg of N), and treatment 4 (N_5K_1C, with 250 kg of N) – for all of these treatments 50 kg of KCl were also added to the crops. To study the effect of the K fertiliser, three treatments were compared (Table 1): treatment 5 (N_3K_0, with 0 kg of KCl), treatment 3 (N_3K_1C, with 50 kg of KCl), and treatment 6 (N_3K_1S, with 50 kg of K_2SO_4) – for all these treatments 150 kg of N fertiliser were also added. ANOVA in Genstat was used to examine differences in three aspects: treatments only, sampling time only and interactions between treatments and sampling

time (treatment & sampling). A probability level of 0.05 was adopted as the confidence level, as it represents a typical confidence level in such studies. Thus, if the Fpr value of treatment, sampling time, and treatment & sampling was less than 0.05, we have assumed that there was at least one pair of treatments or sampling time, or treatment & sampling time interaction, which is significantly different from the others. SED is the *standard error of an estimated difference* and DF is the *number of degrees of freedom* associated with the estimation of the Fpr. The general linear model for regression was also utilised to test relationships between variables in our data.

3. Results and discussions

3.1. Effect of treatments on carbon contents

The means of carbon content for each treatment over the two year sampling period are illustrated in Fig. 1 (3rd year crop) and in Fig. 2 (4th year crop). The SED in these graphs is derived from the interaction between treatment and time. The results show that the C content of Miscanthus (dry basis) is around 47–49%, except for the leaves in treatment 1 of the 4th year crop, which has the

lowest C content (42.10% at the 1st harvest time). It can also be noted that the stems and whole crop have slightly higher C contents than leaves.

For the leaves, significant differences in C content can be observed for the treatments examining the effect of K (treatments 3, 5 and 6) for the 4th year crop only – where treatment 5 shows the highest C content. In contrast, for the stems and whole crop, only the treatments examining the effect of N (treatments 1–4) for the 3rd year crop showed significant differences, with treatment 1 – generally resulting in greater C contents.

With respect to change of C concentrations with sampling times, for leaves, only the treatments examining the effect of varying K fertiliser (treatments 3, 5 and 6) for the 4th year crop showed a decrease in C contents from the 1st to the 2nd sampling. For stems and whole crop in the 3rd year, the C contents in all treatments increased over the sampling period. However, for the 4th year crop, only for treatment 3 the C contents increased over the sampling period.

3.2. Effect of treatments on nitrogen contents

The N contents of the 3rd year stems and whole crop samples were below the detection limit for the elemental analyser (i.e. N < 0.3 wt%). Therefore, their data was discounted from the ANOVA analysis. A plot of the means of the N contents (wt% db) for the treatments studied against sampling time for the 3rd year crop is shown in Fig. 3 for the leaves only. Fig. 4 shows the plot of the mean N content for the 4th year crop against sampling time for leaves, and stems and whole crop. The standard error of difference (s.e.d) for the interaction between treatment and sampling time is also shown on both figures. Results show the N content in Miscanthus varies from <0.3 wt% to 1.87 wt%; with leaves, in general, having higher N content than stems and whole crop.

3.2.1. Differences due to treatment
The impact of the N fertiliser (N effect) show significant differences for both sampling years. The samples from treatment 1 (no N fertiliser applied, N_0K_1C) have the lowest N content, whilst treatment 4 (N_5K_1C) yields higher N contents than treatment 2. There is no statistical evidence to show differences among the treatments 2, 3 and 4. However, for the stems and whole crop of the 4th year crop, there is strong evidence that differences exist due to both N and K fertiliser treatment. The analysis of the fertiliser treatments examining the N effect, show that treatments 1 and 2 (N_0 and N_2) result in lower N contents than treatments 3 and 4 (N_3 and N_5). Whilst for the fertiliser treatments examining the K effect, treatment 5 (N_3K_0) shows the lowest N content from January to March.

3.2.2. Differences due to sampling time
The sampling time has a substantial impact on the N content of both leaves and stems. Both Figs. 3 and 4 show that the N content of Miscanthus leaves, and stems and whole crop decreased from the 1st sampling to the 5th sampling time.

3.3. Effect of treatments on calorific value

Calorific values of all treatments were calculated using the method derived by Friedl et al. [15] and described in Section 2.2. Table 2 shows the treatment means of the calculated CVs. The CV values for Miscanthus (dry basis) are in the range of 18–20 MJ kg^{-1}, except for the 1st sampling of leaves from the 4th year crop, which was lower at 17.04 MJ kg^{-1}. Stems and whole crop in general have slightly higher CV than leaves. CVs are calculated mainly based on the C content of the fuel and hence they are strongly influenced by this.

3.4. Effect of treatments on chlorine and sulphur contents

The treatment means of Cl content over the sampling times are presented in Table 3. Results show that the Cl contents of the Miscanthus samples (wt% dry basis) are <0.5% and it decreases over the sampling period. Increasing nitrogen in the fertiliser does not result in higher Cl content in the fuel when treatments 1–4 are compared. However, slightly higher Cl contents are observed when extra KCl was added into the fertiliser – when comparing the average of treatments 1–4 and treatments 5 and 6 (without additional KCl in the fertiliser).

The treatment means of S content over the sampling period are presented in Table 4. Results show that the S contents (wt% dry basis) are less than 0.2% in Miscanthus. The S content is higher in leaves than stems and it does not seem to be affected by the sampling time. Adding extra sulphur into fertiliser in form of K_2SO_4 (treatment 6) does not result in a significantly higher S content in the fuel when compared to rest of the treatments (Table 4). However, the low concentration of S in the fuel makes the detection of statistical significance unlikely.

3.5. Effect of treatments on ash content

The Miscanthus ash contents have been determined by the British standard method as stated in Section 2.3. Heating the fuel slowly
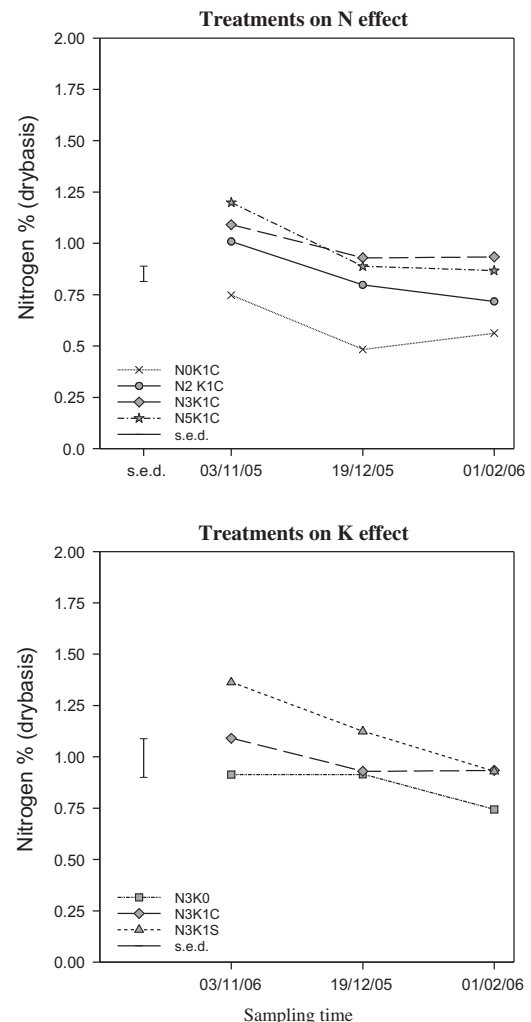

Fig. 3. Plot of the mean N (wt% db) contents of leaves for the different treatments over the sampling period (3rd year crop).

in air to a constant mass at a certain temperature, is the most commonly applied technique for the determination of the ash content of coals and solid biomass fuel in the laboratory. For coal, the standard temperature for ashing is 800 °C. However, for many biomass materials a significant proportion of the inorganic material is very volatile at that temperature (such as K salts). To avoid under estimation of ash content of the fuel, all Miscanthus samples have been heated in air to 550 °C and kept at that temperature for 3 h (no further weight loss was observed after 3 h). Although constant mass was achieved after ashing, a small amount of carbon is believed to remain in the ash due to the low temperature used. The treatment means of all ash contents are presented in Fig. 5 (3rd year crop) and Fig. 6 (4th year crop). The S.E.D (standard error of the difference) for treatment and sampling time (i.e. interaction between treatment and sampling time) has also been included in the plots. Results show that Miscanthus leaves and stems have significant differences in ash contents. In leaves, the average ash content is between 4 and 6 wt% (dry basis). However in stems and whole crop, the average ash content is lower, between 1 and 3 wt% (dry basis).

3.5.1. Differences due to treatment

There is no strong evidence to show treatment differences in leaves over the two-year study. However, in stems and whole crop,

there is evidence of differences for the treatments examining the N effect. For the treatments examining N effect of the 3rd year crop, treatment 3 yields higher ash contents than treatment 1 over all the sampling times. The ash content from treatments 2 and 4 fell between treatments 1 and 3 (Fig. 5), although statistically there is not enough evidence to show this difference. For treatments examining the N effect of the 4th year crop, treatment 1 yields the lowest ash content for the first three sampling times. At the last two sampling times, treatment 4 has the highest ash content, while treatments 1 and 2 have the lowest, and treatment 3 fell between these (Fig. 6). For treatments examining K effect, treatment 5 with no KCl in the fertiliser seems to yield Miscanthus with lower ash content in the 3rd year crop. It seems that the different forms of K (KCl and K_2SO_4) do not result in significant differences in ash contents.

3.5.2. Differences due to sampling time

For leaves, there is a general trend of decreasing ash content in samples from all treatments, especially between the 1st and 2nd sampling time. There are some treatments for which the ash continues to decrease between the 2nd and 3rd sampling times, whilst others show an increase at the 3rd sampling time, as shown in Fig. 5. For stems and whole crop from the 3rd year crop, the ash
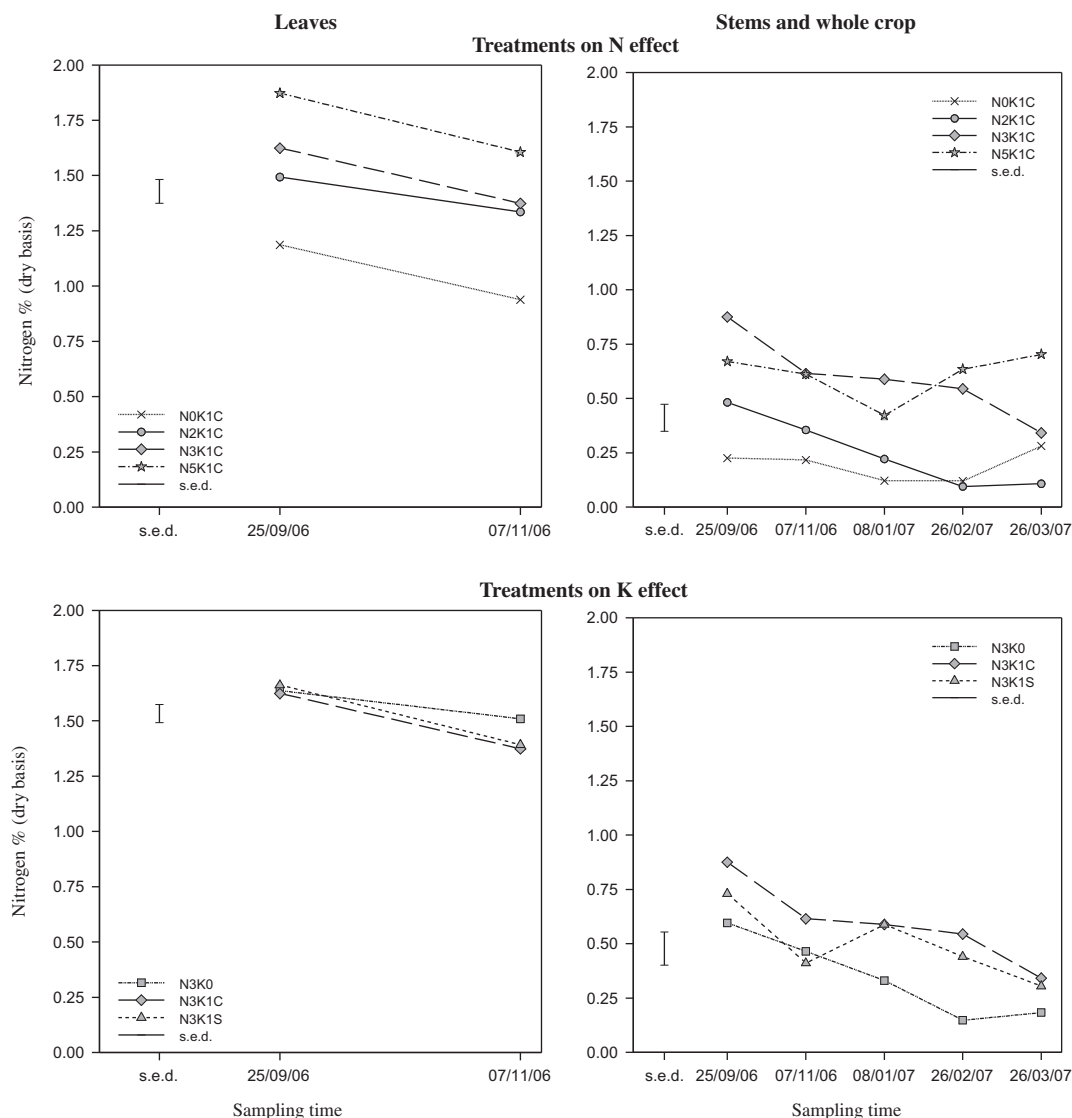

Fig. 4. Plot of the mean N (wt% db) contents of: (a) leaves and (b) stems and whole crops, for the different treatments over the sampling period (4th year crop).

Table 2
Means of calorific value (MJ kg^{-1} db) for the different treatments and sampling times.

3rd year crop		Leaves			Stems		Whole crop		
Sampling time		1st	2nd	3rd	1st	2nd	3rd	4th	5th
1	N_0K_1C	19.42	19.39	19.23	19.47	19.64	19.78	19.82	19.76
2	N_2K_1C	19.32	19.34	19.23	19.37	19.48	19.50	19.53	19.58
3	N_3K_1C	18.84	19.09	18.84	19.11	19.29	19.36	19.33	19.46
4	N_5K_1C	19.49	19.29	19.16	19.28	19.46	19.43	19.53	19.32
5	N_3K_0	19.24	19.33	19.31	19.35	19.38	19.45	19.53	19.77
6	N_3K_1S	19.18	19.51	18.96	19.14	19.34	19.34	19.19	19.32
	Average	19.25	19.33	19.12	19.29	19.43	19.48	19.49	19.54
4th year crop		Leaves		Stems		Whole crop		
Sampling time		1st	2nd	1st	2nd	3rd	4th	5th
1	N_0K_1C	17.04	18.81	19.23	18.68	19.39	19.35	18.97
2	N_2K_1C	19.09	19.14	19.24	19.26	19.14	19.22	19.37
3	N_3K_1C	19.00	18.74	18.98	19.14	19.18	19.31	19.37
4	N_5K_1C	19.53	18.65	19.32	19.33	19.23	18.61	19.20
5	N_3K_0	19.42	19.24	19.38	19.15	19.25	19.45	19.17
6	N_3K_1S	19.10	18.94	19.25	19.17	19.15	19.21	19.32
	Average	18.86	18.92	19.23	19.12	19.22	19.19	19.23

s.e.d and d.f analyses data for this table is in the Supplementary material.

contents in samples from all treatments remain at similar levels over the sampling period. The exception is treatment 5, which produces changes in ash content at different sampling times, as shown in Fig. 5.

3.6. Effect of fertiliser treatments on ash compositions

The ash compositions have been calculated from the metal analysis of the biomass samples, except for SiO_2, which was measured directly in the ash. For these calculations it was assumed that all the metals analysed remain in the ash as stable oxides, such as: SiO_2, K_2O, CaO, MgO, P_2O_5, SO_3, Na_2O, Al_2O_3, Fe_2O_3, and Mn_3O_4. The analysis of these ten major elements expressed as oxides is a reasonable and practical approach for most coals. It has also been applied here for biomass ash, on the assumption that ashes produced by combustion systems are principally in the form of oxides. These ten major elements also reflect the principal inorganic constituents of most biomass materials. As an illustrative example of the findings, the ash composition of Miscanthus leaves (1st sampling), stems (1st sampling) and whole crop (4th sampling) of the 3rd year

crop from treatment 2 (N_2K_1C) are presented in Table 7. It is to be noted that the sum of all the ash constituents did not total 100% for all the samples analysed. These incongruences in the calculated ash composition are due to measurement errors in the analyses (i.e. silica in the ash and metal analysis of samples), and to the assumption that all inorganics are present as oxides, which is not the case for all metals [19]. It can be observed from Table 7 that SiO_2 and K_2O are the two dominant compounds in Miscanthus ash. On average, these two compounds account for 70% of the ash. It can also be noted that K_2O decreases over the sampling period, while SiO_2 increases (not shown). These negative correlations between Si and K are also found in other energy crops [20]. The ashes from Miscanthus leaves have higher CaO and lower K_2O content than ashes from the stems. In general, the sum of Na_2O, Al_2O_3, Fe_2O_3, and Mn_3O_4 comprised less than 1% of the ash.

Ash compositions determine how ash behaves in the boiler. The ash compositions of the whole crop show significant differences to those of coal [2]. Ash compositions of coal vary with coal rank [21]. Nevertheless, the main difference is that Miscanthus ash has a much higher K_2O content and lower Al_2O_3 and Fe_2O_3 contents than

Table 3
Means of Cl content (wt% dry basis) for the different treatments and sampling times.

3rd year crop		Leaves			Stems		Whole crop		
Sampling time		1st	2nd	3rd	1st	2nd	3rd	4th	5th
1	N_0K_1C	0.29	0.05	0.03	0.23	0.12	0.11	0.13	0.18
2	N_2K_1C	0.30	0.06	0.03	0.20	0.24	0.20	0.16	0.22
3	N_3K_1C	0.30	0.08	0.05	0.29	0.23	0.26	0.21	0.13
4	N_5K_1C	0.29	0.08	0.04	0.22	0.22	0.20	0.17	0.30
Average of 4 treatments		0.30	0.07	0.04	0.24	0.20	0.19	0.17	0.21
5	N_3K_0	0.10	0.05	0.02	0.12	0.10	0.07	0.07	0.05
6	N_3K_1S	0.11	0.06	0.03	0.10	0.09	0.08	0.07	0.09
4th year crop		Leaves		Stems		Whole crop		
Sampling time		1st	2nd	1st	2nd	3rd	4th	5th
1	N_0K_1C	0.52	0.46	0.30	0.25	0.14	0.08	0.04
2	N_2K_1C	0.49	0.46	0.33	0.28	0.18	0.13	0.17
3	N_3K_1C	0.46	0.44	0.43	0.32	0.22	0.19	0.17
4	N_5K_1C	0.38	0.38	0.40	0.29	0.22	0.20	0.18
Average of 4 treatments		0.46	0.44	0.37	0.29	0.19	0.15	0.14
5	N_3K_0	0.15	0.19	0.13	0.11	0.07	0.06	0.06
6	N_3K_1S	0.14	0.17	0.11	0.09	0.06	0.06	0.03

s.e.d and d.f analyses data for this table is submitted as "additional material".

Table 4
Means of S content (wt% dry basis) for the different treatments and sampling times.

3rd year crop		Leaves			Stems			Whole crop	
Sampling time		1st	2nd	3rd	1st	2nd	3rd	4th	5th
1	N_0K_1C	0.08	0.10	0.12	0.02	0.03	0.02	0.02	0.02
2	N_2K_1C	0.10	0.12	0.13	0.03	0.03	0.04	0.04	0.03
3	N_3K_1C	0.09	0.11	0.13	0.03	0.03	0.03	0.04	0.07
4	N_5K_1C	0.10	0.12	0.15	0.23	0.03	0.03	0.04	0.03
Average of 4 treatments		0.09	0.11	0.13	0.08	0.03	0.03	0.04	0.04
5	N_3K_0	0.10	0.12	0.13	0.03	0.03	0.03	0.04	0.02
6	N_3K_1S	0.11	0.12	0.14	0.04	0.05	0.06	0.06	0.05
4th year crop		Leaves		Stems		Whole crop			
Sampling time		1st	2nd	1st	2nd	3rd	4th	5th	
1	N_0K_1C	0.10	0.09	0.03	0.03	0.02	0.04	0.01	
2	N_2K_1C	0.12	0.11	0.04	0.04	0.04	0.03	0.05	
3	N_3K_1C	0.12	0.12	0.04	0.03	0.04	0.05	0.03	
4	N_5K_1C	0.13	0.12	0.04	0.03	0.03	0.04	0.02	
Average of 4 treatments		0.12	0.11	0.04	0.03	0.03	0.04	0.03	
5	N_3K_0	0.13	0.12	0.04	0.04	0.04	0.04	0.03	
6	N_3K_1S	0.14	0.13	0.07	0.07	0.06	0.05	0.04	

s.e.d and d.f analyses data for this table is submitted as "additional material".
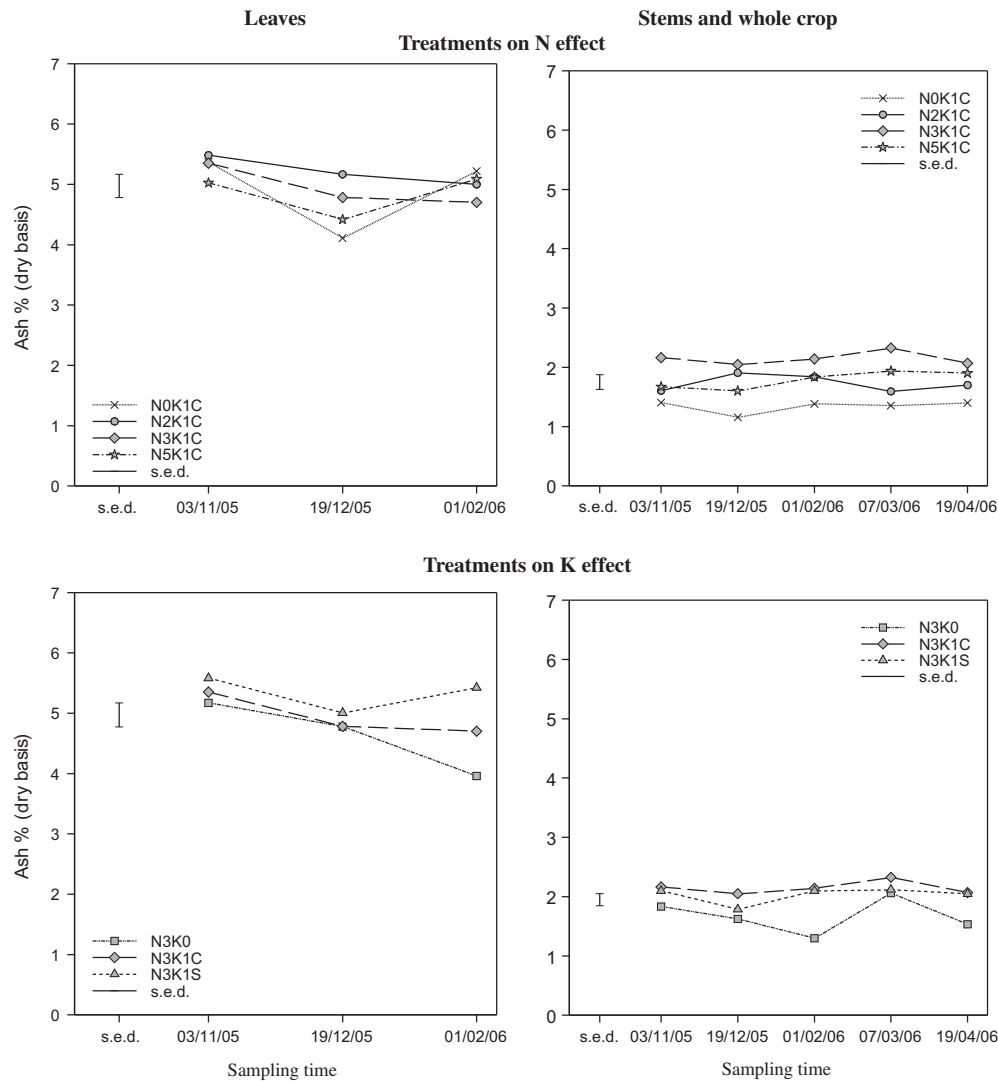

Fig. 5. Plot of the mean ash (wt% db) contents of: (a) leaves and (b) stems and whole crops, for the different treatments over the sampling period (3rd year crop).

a typical bituminous coal ash. It is also noticeable that Miscanthus has quite a high P content compared to typical coal ash. The P_2O_5 content of the ash can be over 10% depending on treatments and sampling time (data not shown). Such high P content is also found in other biomass ash, such as barley straw and corn stalks [7]. The silica content of the whole crop is lower than values reported by other researchers (e.g. 50–69% in Kludze et al. [22]), and the K_2O content is higher, but most of the sampling here has been carried out on immature crops and also the different agronomy treatments are expected to have an impact on their mineral content, especially on the K concentrations.

3.7. Effect of treatments on slagging and fouling indices

A number of indices have been developed for predicting fouling and slagging behaviour of coal. The majority of these indices are based either on or ash composition or on the assessment of the fusion behaviour of alumino-silicate in coal ash. Coal fouling indices are, in the main, based on sodium compound depositions by volatilisation or condensation mechanisms. Potassium content in coal ash is mainly presented as a constituent of the clay minerals [23]. This is not considered to be available to be released by

volatilisation in the flame. However for most biomass materials, potassium is the dominant alkali metal, and is generally present in a volatile form [23,24]. Despite the problems, a suite of coal ash characterisation techniques and predictive indices, such as alkali index and base to acid ratio, are available for biomass materials, because they are already familiar to industry and likely to provide a secure basis when it comes to decision-making.

3.7.1. Effect of fertiliser treatments on alkali indices

The alkali index has proved useful and thus became popular in recent years for biomass as the threshold indicator for fouling. The alkali index (AI) expresses the quantity of alkali oxide in the fuel per unit of fuel energy (kg alkali GJ^{-1}), as given by the following equation:

$$AI = \frac{kg(k_2O + Na_2O)}{GJ} \qquad (E.2)$$

It has been suggested that index values in the range of 0.17–0.34 kg/GJ indicate that fouling is probable, and above 0.34 fouling is virtually certain to occur [2]. Alkali indices of Miscanthus treat-
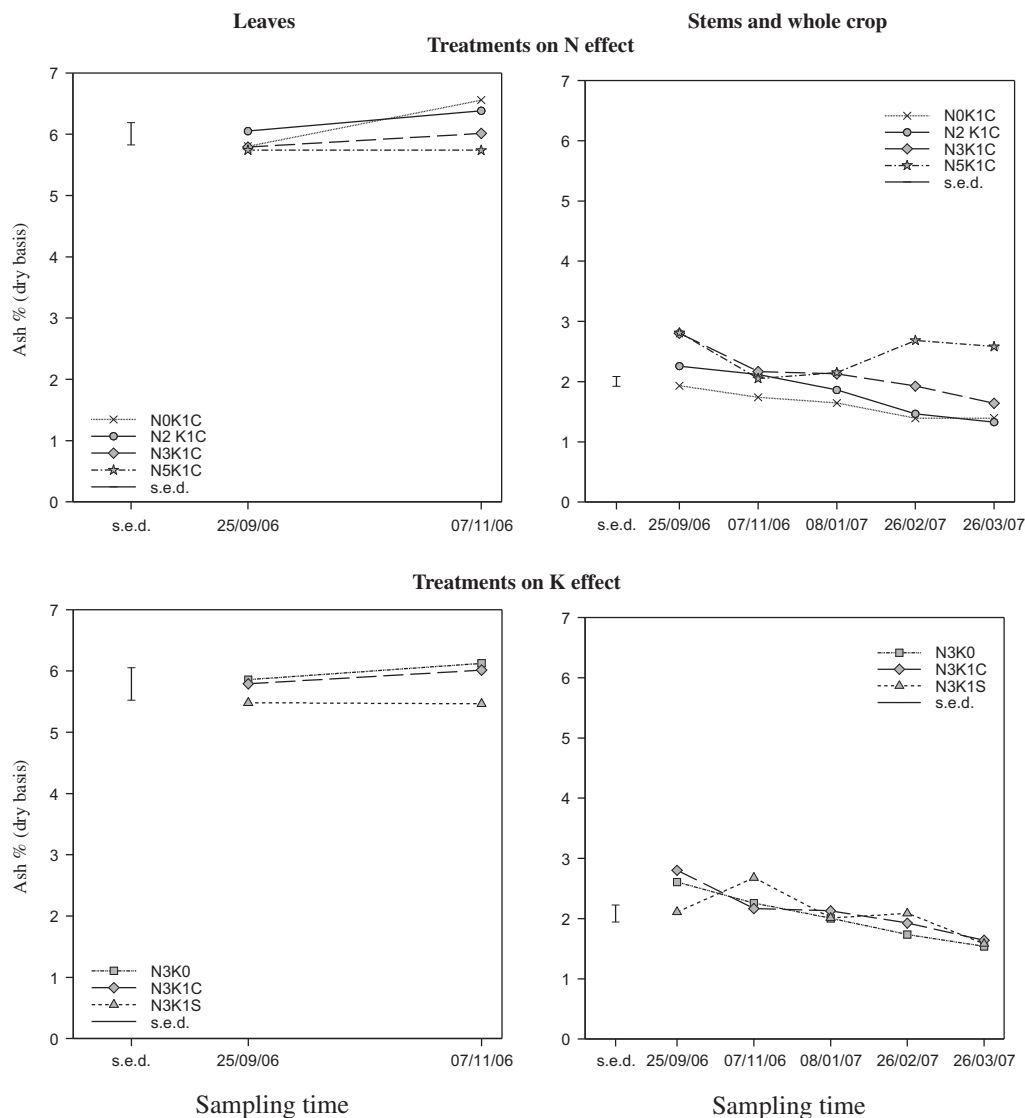

Fig. 6. Plot of the mean ash (wt% db) contents of: (a) leaves and (b) stems and whole crops, for the different treatments over the sampling period (4th year crop).

ment means are illustrated in Fig. 7 (3rd year crop) and Fig. 8 (4th year crop). Results show that for this Miscanthus crops the alkali index generally decreases over the sampling period. The highest alkali index observed in the average of treatment means is 0.76 kg alkali/GJ and the lowest is 0.13 kg alkali/GJ. The alkali index is based on the K and Na contents of the biomass fuel. Compared to K_2O, the Na_2O content in Miscanthus is very low (less than 1%). So the alkali index of Miscanthus is actually mainly dependent on the K_2O per unit energy.

3.7.1.1. Differences due to treatment. Results show that treatment 1, examining N effect, yields the lowest alkali index in both leaves and stems and whole crop over the two year sampling period. The differences among the treatments, when examining the K effect, were not significant.

3.7.1.2. Differences due to sampling time. The sampling time has a significant impact on the alkali index for all treatments (Fpr <0.05). For all treatments studied, the alkali index is the highest at the time of the 1st sampling and drops to the lowest value by the 5th sampling time.

3.7.2. Effect of treatments on base to acid ratios
The base-to acid ratio (B/A) has been used as a measure of the slagging tendency of a biomass ash, although its interpretation

appears to be different to that of coal [2]. This ratio takes the form given in equation:

$$R_{B/A} = \frac{\%(Fe_2O_3 + CaO + MgO + K_2O + Na_2O)}{\%(SiO_2 + TiO_2 + Al_2O_3)} \tag{E.3}$$

All treatment means of base to acid ratio are illustrated in Fig. 9 (3rd year crop) and Fig. 10 (4th year crop). Results show leaves have lower base to acid ratio than stems. In leaves, the average values for all treatments are between 0.7 and 1.6. In stems and whole crop, the averages are higher – between 1.3 and 3.2. Thus indicating that leaves have a lower slagging propensity than stems and whole crops. Base to acid ratios were developed for predicting ash slagging behaviour for coal combustion, where: a B/A < 0.5 indicate a low risk of slagging, a B/A in the range of 0.5–1.0 indicate a medium risk, whilst a B/A between 1.0–1.75 is for a high to severe risk [21]. However a review from Jenkins et al. [2] suggested that the relationship between melting temperature of ash with base to acid ratio tends to be parabolic – reaching a minimum at intermediate values. Previous work on the ash melting behaviour of Miscanthus agreed with the latter, since a parabolic relationship was found for both, B/A and base percentage, with respect to ash melting temperature [17].

3.7.2.1. Differences due to treatments. There is no evidence of differences in base to acid ratios between treatments when examining
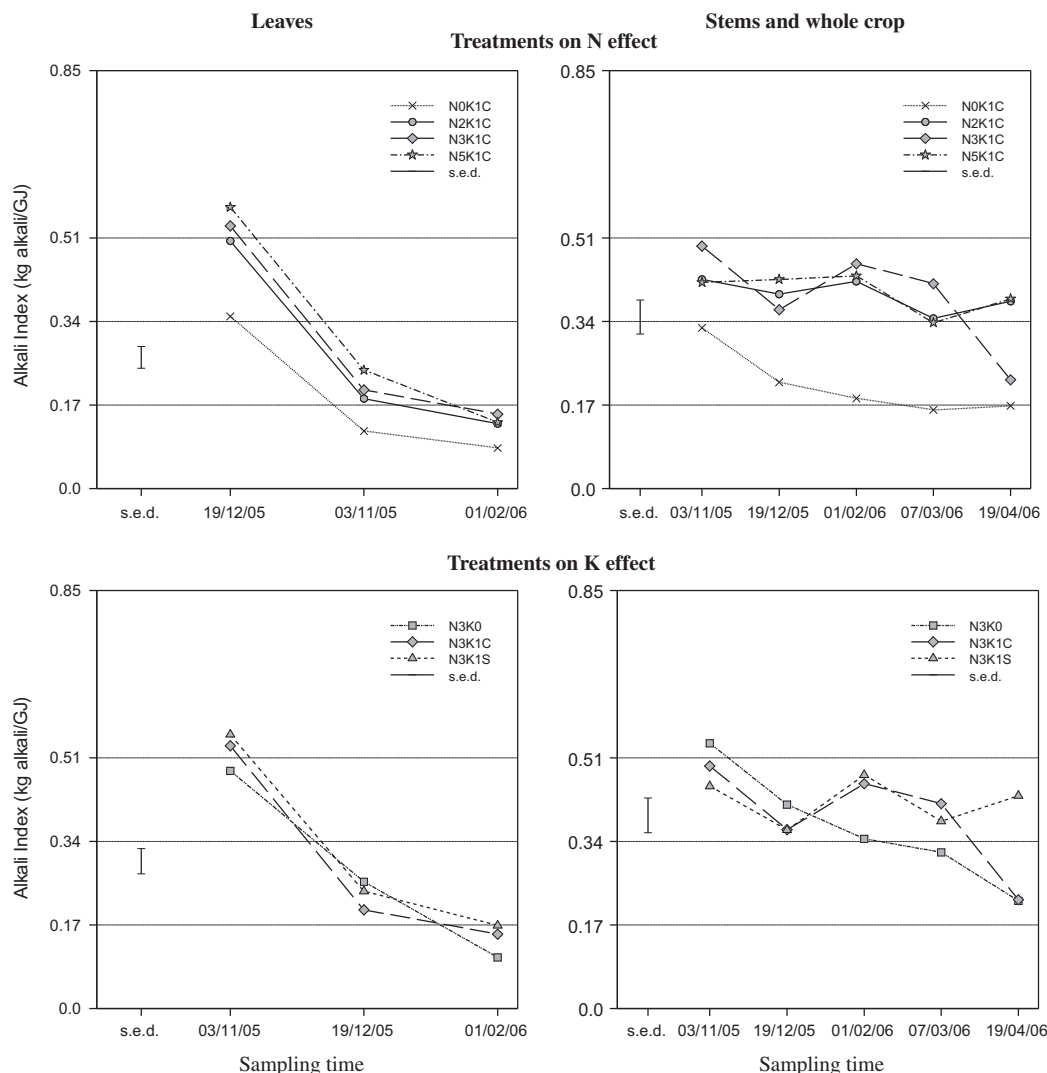

Fig. 7. Variation of alkali index (treatment mean) over the sampling period for the 3rd year crop.

the effect of K. However, the differences between treatments when examining the N effect are significant. Treatment 4 (N_5K_1C) yields ashes with higher base to acid ratios than treatment 1 (N_0K_1C) at all sampling times over the two-year study. The base to acid ratios of ashes from treatments 2 and 3 fall between those from treatments 1 and 4, although the differences are not statistically significant.

3.7.2.2. Differences due to sampling time. Results show that all the treatments considered yield ashes with a higher base to acid ratio when first sampled, and then the B/A drops gradually over the sampling period. This is significant for all leaves and stems and whole crop over the two-year growth. It should be noted that only in the case of treatment 1 (N_0K_1C), the B/A fell below the threshold for low slagging propensity (i.e. <0.5).

3.8. Effect of treatments on overall fuel quality

A summary of the results from the statistical analysis of the different agronomy treatments and sampling times and their effect on fuel characteristics of Miscanthus, such as: C, N, Cl, S concentrations, ash content, ash composition and resultant slagging and fouling indices and CV is presented in this section.

3.8.1. Differences between leaves and stems

Overall the fuel characteristics of the Miscanthus stems are better than leaves. The stems have much lower ash, N and S contents, and slightly higher C (and hence higher CVs). Although, leaves from late sampled Miscanthus have a lower propensity for slagging than stems, due to their lower K content.

3.8.1.1. Effect of fertiliser treatments. Regarding the treatments examining the N effect, increasing N in the fertiliser results in higher N and ash contents in the resultant fuels. Therefore, treatment 1 (N_0K_1C) yields a fuel of better quality than the others – with lower N, ash content, fouling indices, and slightly higher C contents. Although, there is no statistical evidence to show that increasing N from 100 to 250 kg ha^{-1} in the fertiliser increases the fouling propensity of the fuel ash. Regarding the treatments examining K effect: treatment 5 (N_3K_0, without any added KCl in the fertiliser) yields Miscanthus with slightly lower N content, higher C in the leaves from the 4th year crop, and lower ash content of the 3rd year crop. Treatment 5 (K effect) produces very similar results to treatment 1 (N affect). It has been suggested that the forms of K (KCl and K_2SO_4) do not result in significant differences on C, N, S, ash contents and fouling indices in the fuel. However, a slight increase in the Cl content of the crop was observed when K was added in the form of KCl.
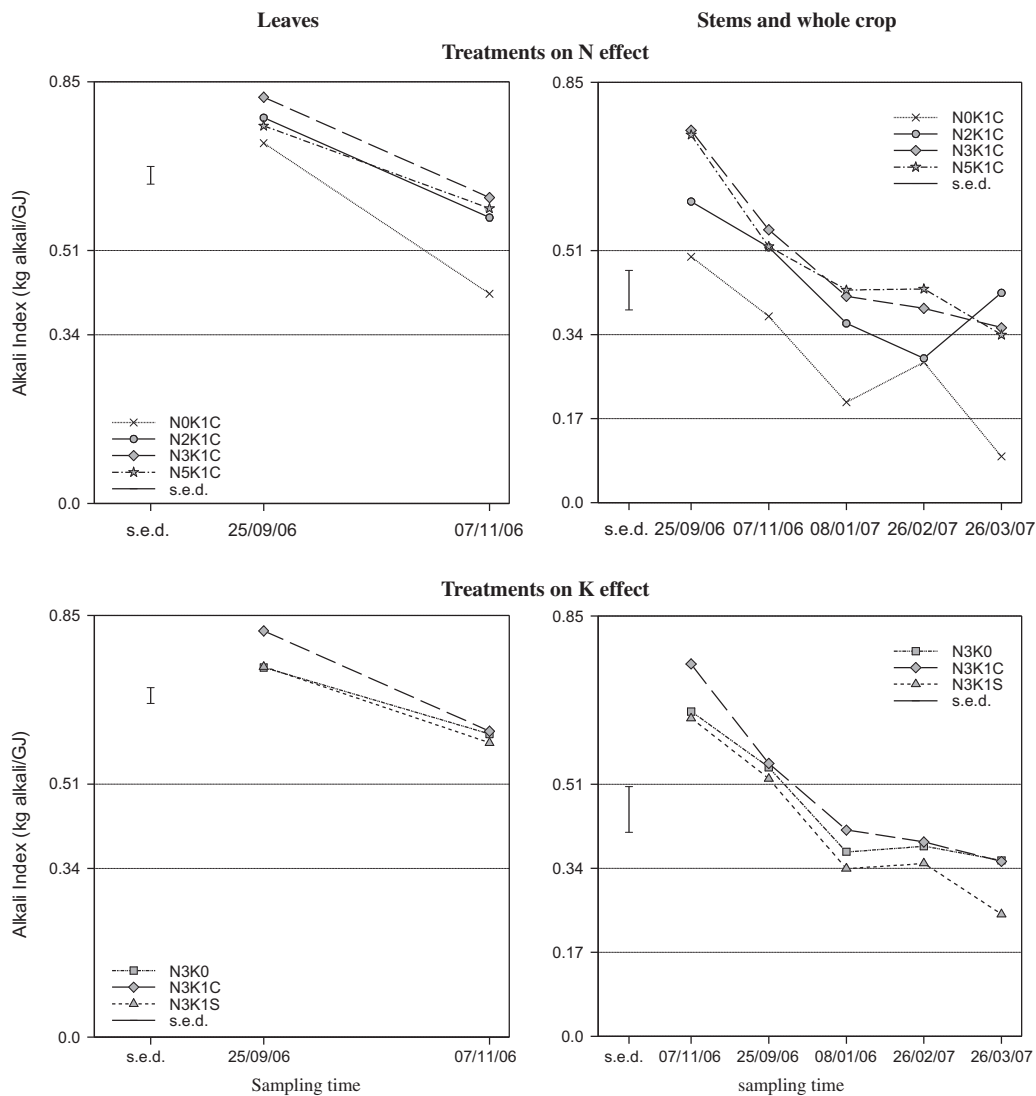

Fig. 8. Variation of alkali index (treatment mean) over the sampling period for the 4th year crop.

3.8.1.2. Effect of sampling time. Miscanthus was sampled five times over the autumn/winter for a period of two years. At each sampling time, a 1 m square area of Miscanthus crop over 10 × 12 m plot was cut for assessing the yield and other analysis. When comparing the changes at different sampling times, theoretically we need to assess the same samples at different sampling times. However, this is not practical for Miscanthus sampling. It is assumed that the difference due to sample time is greater than the spatial variation within a plot. Furthermore, errors are also reduced by using a randomised block design with three replicates. So, with these assumptions and considerations, in general, late harvested Miscanthus samples have better fuel quality, with lower N, Cl, K, ash contents, alkali index and slightly higher C contents. However, with the exception of treatment 1, all other treatments fell within the 'fouling possible' to 'fouling certain to occur' regions. These results suggest that fouling could be an issue for Miscanthus when additional N is used in the fertiliser in order to improve yield. Some fuel pre-treatment (such as leaching, additives) and boiler system change (i.e. combustion techniques and flue gas temperature) may be needed to avoid ash related problems occurring during Miscanthus combustion.

3.8.1.3. Effect of growth year. Results from this work show there is no significant differences for C, N and ash content over two growth years, when comparing average data of all treatments at similar sampling time. At least one more growth year is needed to statistically identify whether fuel quality is affected by growth year.

3.9. Combustion properties

3.9.1. Volatile peak temperature

The fuel combustion rate is a very important factor in the design of combustion systems. Fundamental to the combustion rate are the rates of fuel pyrolysis and char oxidation. Samples from all the Miscanthus treatments, in their triplicates have been investigated for their combustion behaviour by TGA. Results show that Miscanthus volatile combustion occurs between 300 and 400 °C A sub-set of samples was repeated to test the repeatability. The repeatability for the temperature of maximum rate of volatile combustion was found to be ±2.8 °C. The volatile combustion peak temperature represents the point of maximum rate of mass loss. Treatment means of peak temperatures are presented in Figs. 11 and 12 for the 3rd and 4th year crop, respectively. Results show that on average, leaves have slightly higher volatile combustion peak temperatures than stems and whole crop. The volatile combustion peak temperature is between 319–349 °C in leaves and 312–342 °C in stems and whole crop. There is no interaction between treatments and sampling time.
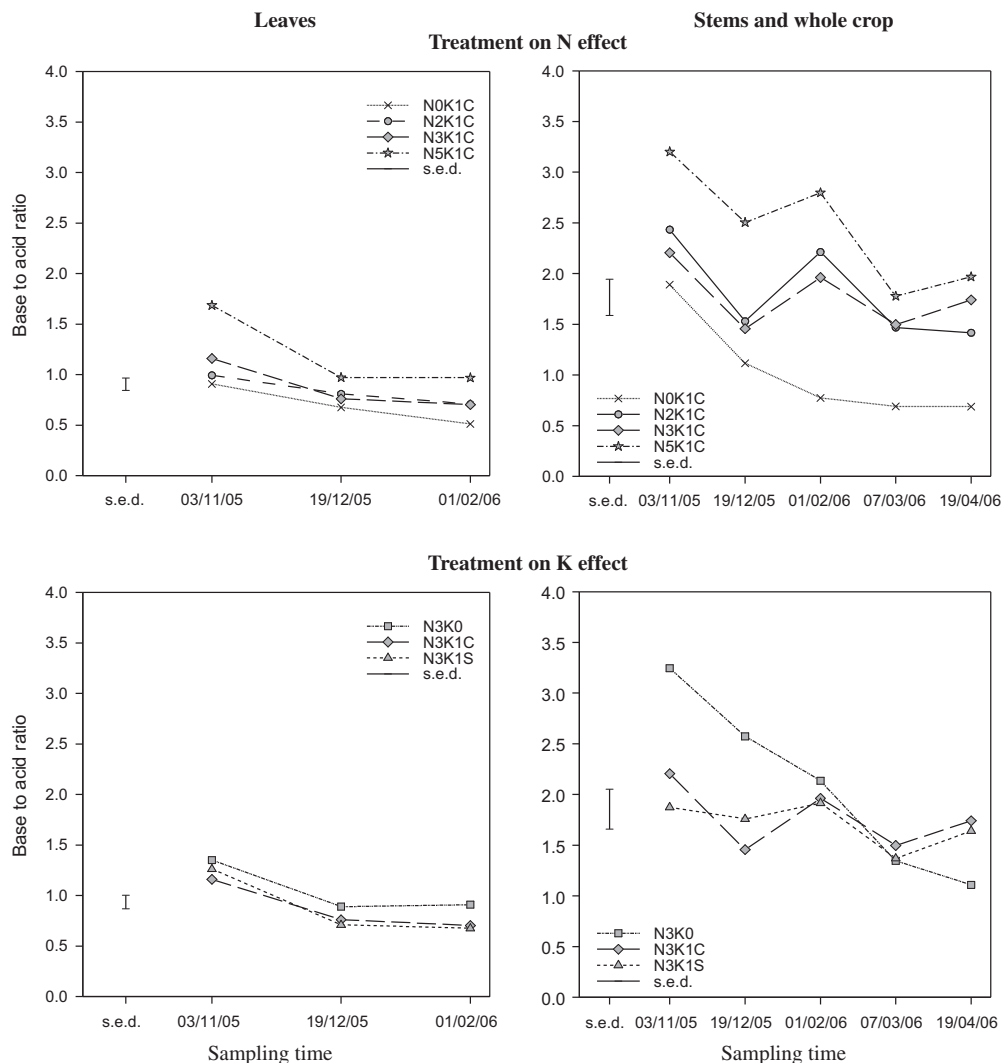

Fig. 9. Variation of base to acid ratio (treatment means) over the sampling period for the 3rd year crop.

3.9.1.1. Effect of fertiliser treatments. When examining the N effect for both years, the stems and whole crop from treatment 1 yields a fuel with the highest volatile combustion peak temperature (with exception of the first sampling time). There is not enough statistical evidence to show any treatment differences for the rest of the treatments.

3.9.1.2. Effect of sampling time. The time of sampling has a strong influence on the peak temperature for volatile combustion in some of the treatments. There is an increasing trend for volatile combustion peak temperature over the sampling period for some treatments. For example, the volatile combustion peak temperature in leaves increased from the 1st to 2nd sampling for all treatments; for stems and whole crop from the 4th year crop, the volatile combustion peak temperature increased over the sampling period for all treatments. However, for stems and whole crop at 3rd year crop, only treatment 1 showed an increasing trend over the sampling time.

The above results are based on statistical analysis of replicate samples only, which give a good estimate of background variation against each treatment, to judge treatment differences. Measurement errors are excluded in ANOVA analysis as it is assumed the estimate of background error (from triplicates) is larger than measurement error for each sample. For the volatile combustion peak temperature, the measurement error is ±2.8 °C (standard

deviation). The above conclusions for the comparisons of treatments are still valid when considering this measurement error. For instance, the stems and whole crop from treatment 1 (N effect) still yields a fuel with the highest volatile combustion peak temperature (with exception of the first sampling time) when considering the measurement error of ±2.8 °C.

3.9.2. Correlations for mineral matter and volatile peak temperature: Pearson's correlation test

Understanding the relationships among minerals and volatile combustion peak temperature is important, as the catalytic effect of some minerals on volatile combustion peak temperature can also depend on the concurrent presence of others. The variance between experimental units (replicates) may be exploited by dropping the experimental design and analysing the data set using each experimental unit as an individual data point. Table 5 lists the correlation coefficients (r) found for the relationships between minerals and volatile combustion peak temperatures, which have been performed using the *Pearson's correlation test* and individual experimental units. A number of significant correlations have been found for both Miscanthus leaves and stems.

In leaves, the volatile combustion peak temperatures have a strong negative relationship to K (-0.7621) and P (-0.7739), but a positive relationship to Na (0.6439). Potassium also has a strong positive relation to P (0.9491) and a negative relation to Na
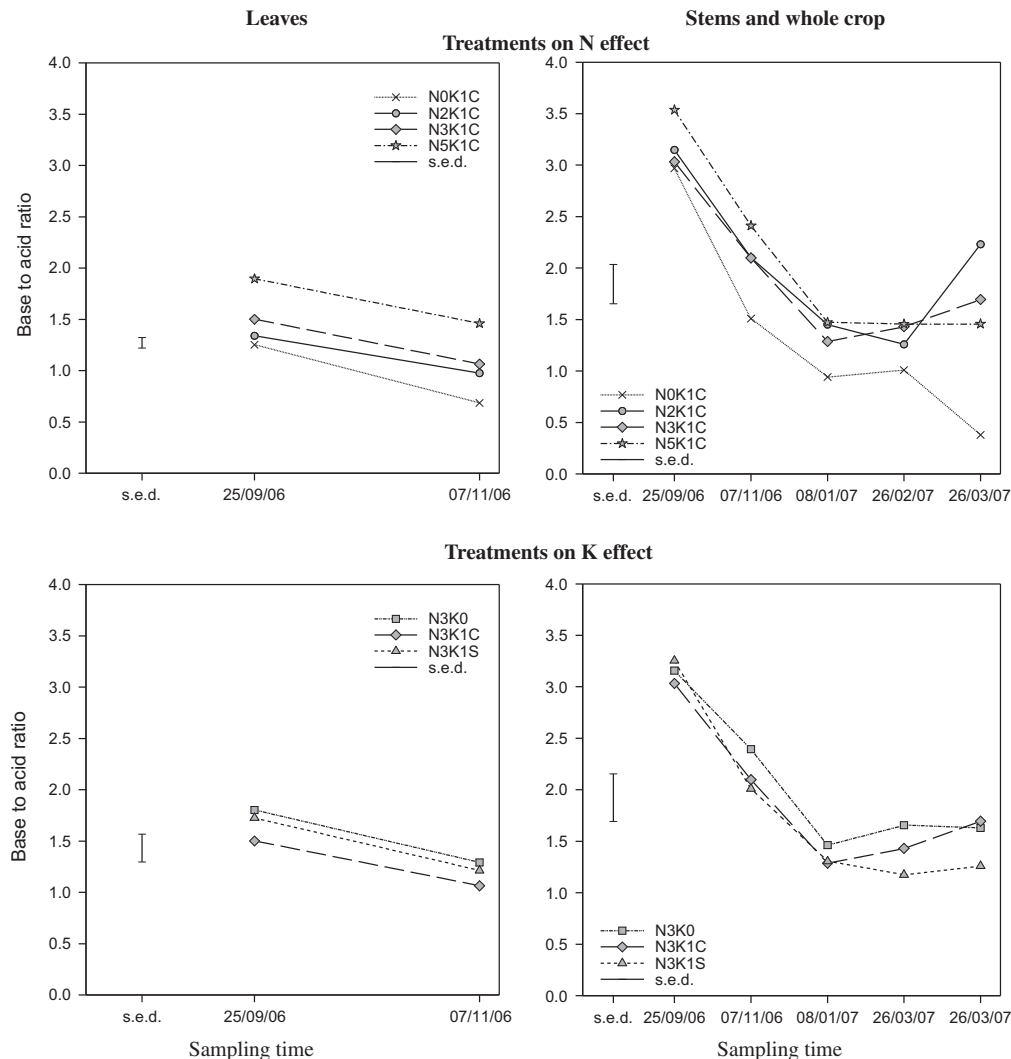

Fig. 10. Variation of base to acid ratio (treatment means) over the sampling period for the 4th year crop.

(−0.8387). Na and P are also highly related (−0.8532). However in stems, the volatile combustion peak temperatures are only related to K (−0.6456). Ca, Fe and Na have a strong positive relationship among them. It is apparent that mineral concentrations and partitions have significant differences in different parts of Miscanthus (leaves and stems). Similar results have also been found for other energy crops [20].

The correlations between volatile combustion peak temperatures and each element are also illustrated in Fig. 13. Potassium has strong correlations with volatile combustion peak in both leaves and stems. Phosphorous has strong correlations with volatile combustion peak temperature only in leaves. Sodium seems to have positive correlations with peak volatile in leaves, but this is discussed further below. According to the metal analysis, K is the dominant compound (apart from silicon), so the influence of K on volatile combustion peak temperature is the strongest.

A catalytic influence of K and P on devolatilisation peak temperature is expected, but these results illustrate that the magnitude of this influence depends not only on their concentrations in Miscanthus, but also on whether we are considering leaves or stems. The reason for this is unclear at present. We can speculate that it is associated with the form of the element in the biomass, and that there is a synergy with other elements (e.g. between K and P), or

the plant elements within the biomass bio-polymers. It is interesting that no such catalytic correlation is observed for sodium, since this has been shown to have similar catalytic potency to K. However, it should be noted from Fig. 13 that the concentration range for Na is much lower than for K, and that the limit in concentration range may not reveal the full relationship with devolatilisation peak temperature. This is true for the other metals at low concentrations also. The errors associated with the correlations are discussed in the following section.

3.9.3. Correlations for mineral matter and volatile peak temperature: Linear regression

Previous sections reviewed how leaves and stems contain different minerals and correlations; also how each mineral correlate to volatile peak temperatures. Here, linear regression was used to investigate how the total metal concentrations correlate to volatile peak temperatures.

3.9.3.1. Correlations for leaves and stems. Relationships between mineral matter contents and volatile peak temperature for the Miscanthus components were analysed by applying the Generalised Linear Regression model (Block + Metals * Parts). Although not all the metals show strong relationships to volatile combustion
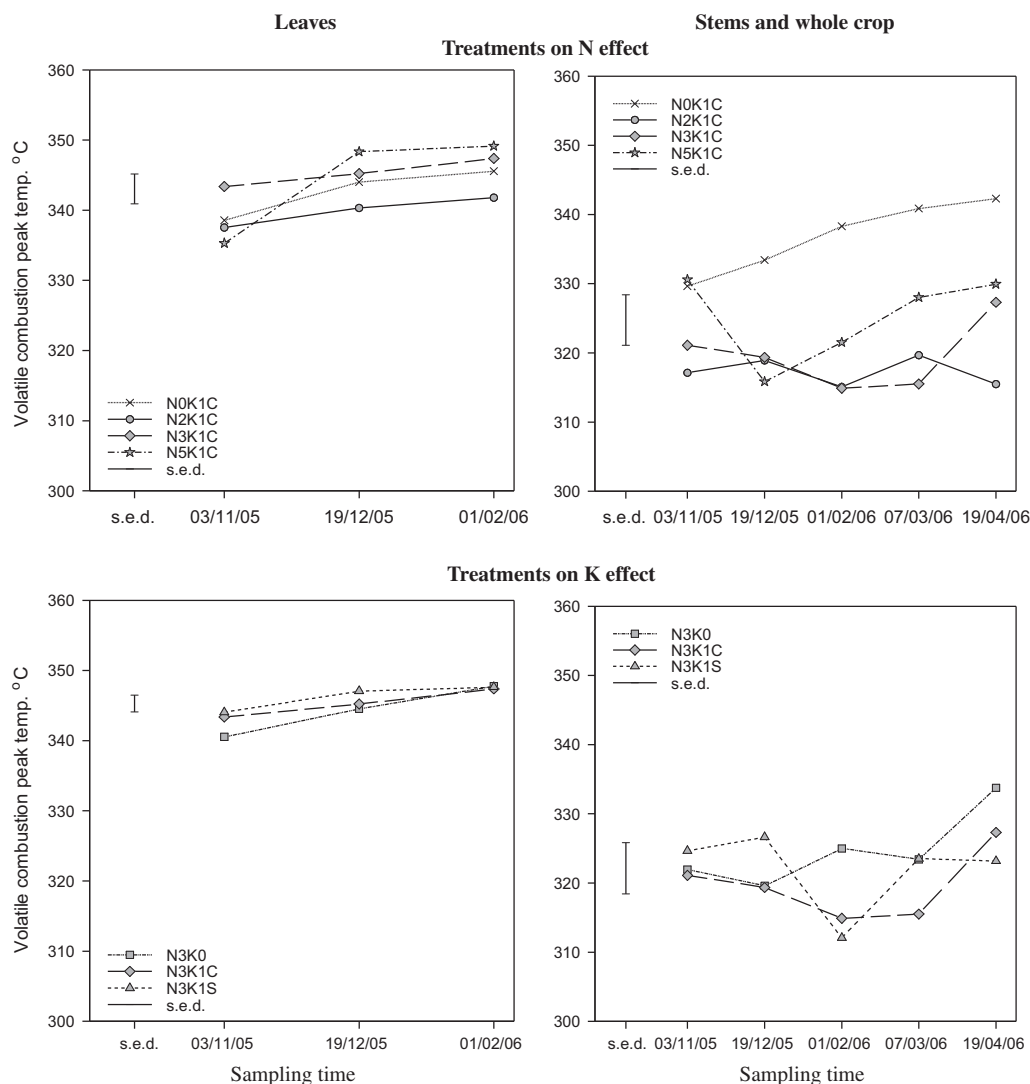

Fig. 11. Volatile combustion peak temperature (treatment means) over the sampling period for the 3rd year crop.
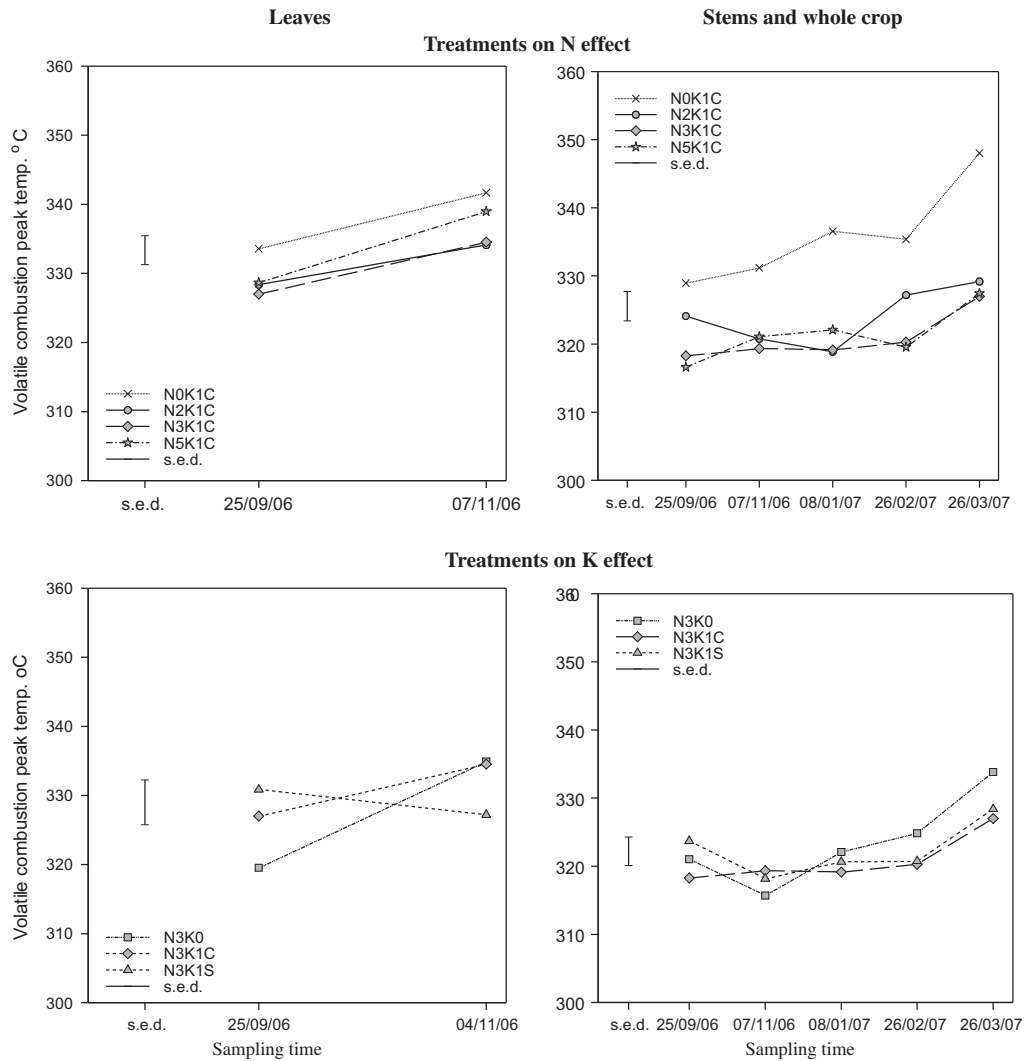
Fig. 12. Volatile combustion peak temperature (treatment means) over the sampling period for the 4th year crop.

Table 5
Correlation coefficients between the peak temperature for volatile combustion for Miscanthus leaves and stems and their elemental contents.

Part	$T_{volatile}$	Ca	Fe	K	Mg	Na	P
Leaves							
$T_{volatile}$							
Ca	−0.0313						
Fe	0.4751	0.2495					
K	−0.7621	−0.0357	−0.6178				
Mg	−0.3153	0.0776	−0.0956	0.4856			
Na	0.6439	−0.0340	0.5060	−0.8387	−0.4885		
P	−0.7739	0.0549	-0.5763	0.9491	0.3984	−0.8532	
Stems							
$T_{volatile}$							
Ca	−0.0338						
Fe	0.0373	0.8236					
K	−0.6456	−0.0420	−0.1817				
Mg	−0.3855	0.5847	0.3477	0.4596			
Na	0.1635	0.6265	0.7529	−0.3099	0.1360		
P	−0.0579	0.1652	0.0455	0.4691	0.1568	−0.1108	

peak temperatures, it appears that the volatile combustion peak temperature is related to total metal contents and their concentrations. Fig. 14 shows the relationship between the total main metals and volatile combustion peak temperature. Percentage variance is

accounted for how much of the variability of the data can be explained by a fitted regression model. A higher percentage variance accounted for a better linear fit with all the data [18]. Separate lines models have been applied to leaves and stems as there is a

significant difference between total metals and Miscanthus parts (Fpr < 0.001). Blocking seems to also have an influence on the volatile combustion peak temperature (Fpr < 0.001). The reasons for the differences between blocks could not be elucidated from current research; it is possible that these differences could be due to the environmental conditions, such as variability across the experimental field, i.e. the degree of exposure to weathering.

3.10. Leaves

The results from the regression analysis examining the influence of agronomic treatments on the metal contents of Miscanthus leaves are illustrated in Fig. 15. The regression equations for each treatment are presented in Table 6. The different Miscanthus agronomy treatments did not result in volatile combustion peak
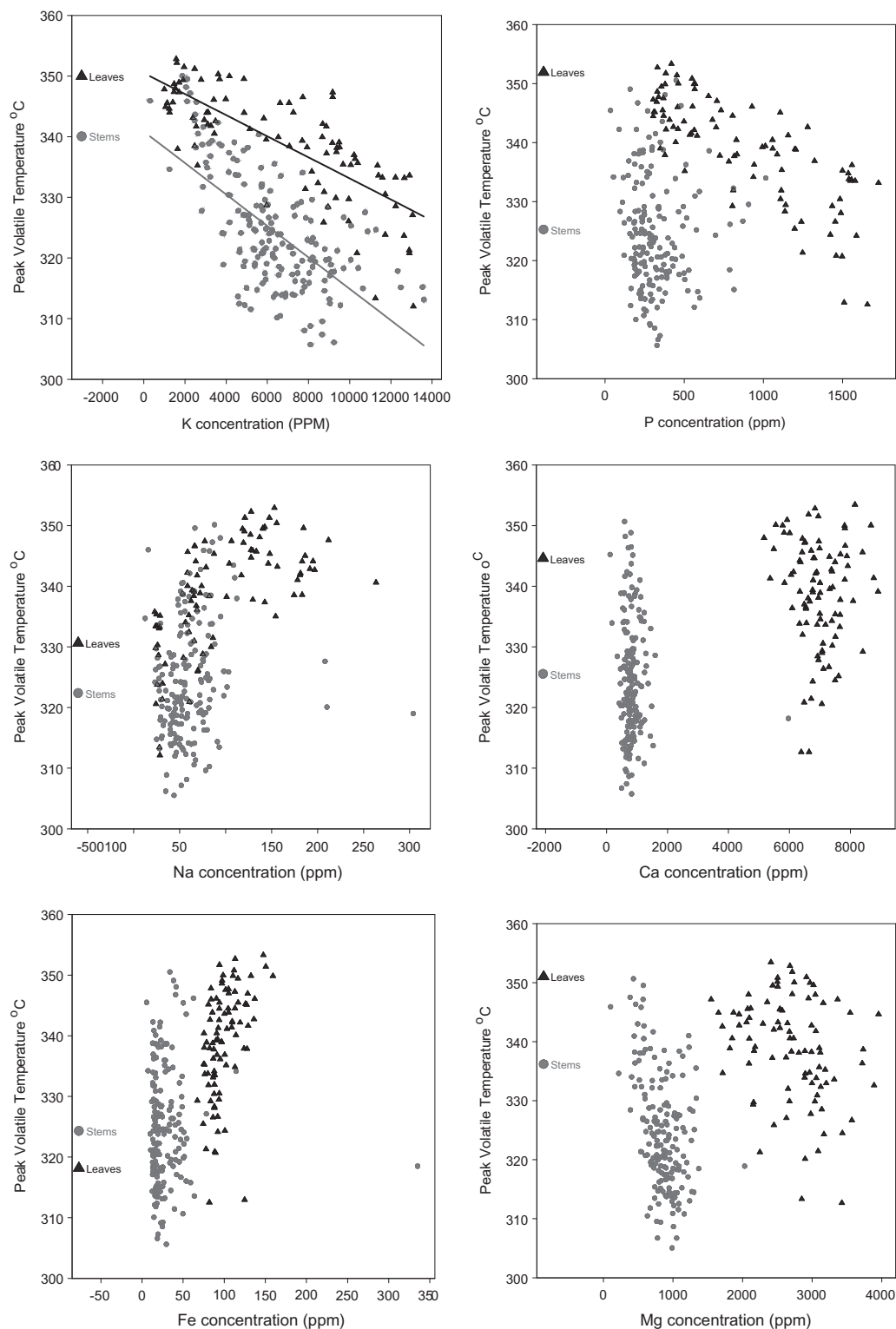

Fig. 13. Correlations between volatile combustion peak temperatures and each of the major inorganic elements in Miscanthus, separated in leaves and stems.
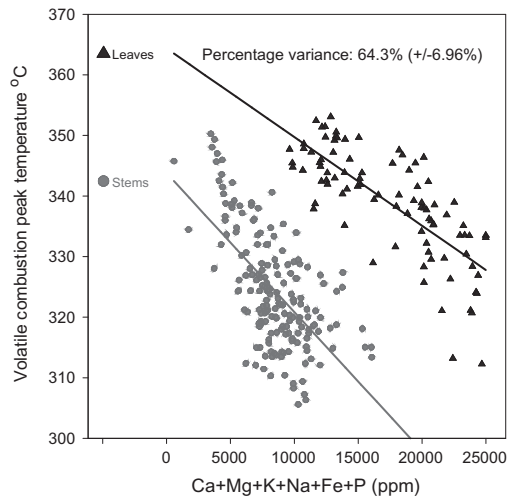
Fig. 14. Relationship between volatile combustion peak temperatures and total concentrations of the main elements in Miscanthus leaves and stems (where stems means stems and whole crop).
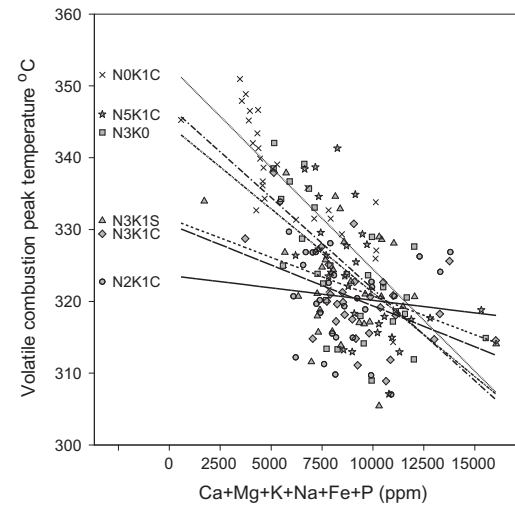

Fig. 16. Separated lines regression model for volatile combustion peak temperatures and total metals in Miscanthus stems and whole crop for each treatment.
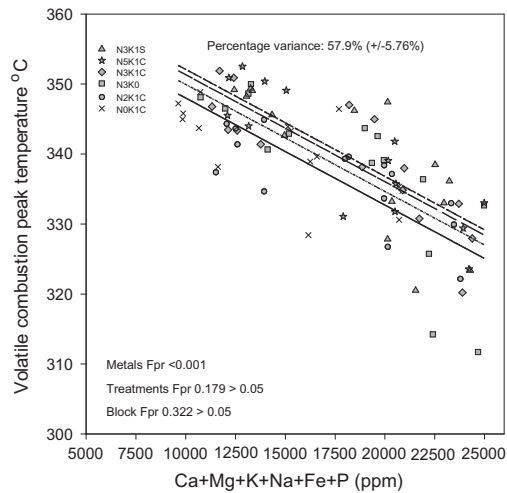
3.11. Stems and whole crop

The results from the regression analysis examining relationships between volatile combustion peak temperatures, metals and treatments for Miscanthus stems and whole crop are presented in Fig. 16. The regression equations for each treatment are presented in Table 6. Each treatment is seen to have a different correlation with volatile combustion peak temperature (Fpr of metals treatment <0.05), so different intercepts and slopes are reported for each treatment in Table 6. In contrast to the results for leaves, treatments 1, 4 and 5 seem to produce stronger correlations between metal concentration and volatile combustion peak temperature than treatments 2, 3 and 6 for stems and whole crops.

A simple linear regression within groups of data in GenStat is a useful tool to distinguish different patterns of response in the Miscanthus treatment trials. All linear regression models presented in this work show strong relationships between metal contents in different parts of Miscanthus and volatile combustion peak temperatures. Results also revealed that agronomy treatments differences did not result in volatile combustion peak temperature differences in Miscanthus leaves (a single linear regression could be applied for all 6 treatments). However, for stems and whole crop, each treatment is seen to have a different correlation with volatile combustion peak temperature (different intercepts and slopes are reported for each treatment). The reason for the difference in leaves and stems among the treatments is unclear at present. A possible reason could be due to the mobility of metals. Metals are more mobile in leaves than stems and whole crop for

Fig. 15. Regression model for the volatile combustion peak temperatures and total metals in Miscanthus leaves for each treatment.

temperature differences (Fpr > 0.05). In this instance, a single linear regression was applied for all 6 treatments. The procedure for this regression analysis involved first applying a separate line among treatments; if there are no significant differences then a single linear regression was applied to all treatments.

Table 6
Predictive equations for the linear regressions of the peak temperature for volatile combustion and total metals in Miscanthus leaves and stems and whole crop (Y = estimate intercepts (s.e) + slope (s.e) * X).

Treatments	Leaves				Stems and whole crop			
	Slope	s.e.	Estimate intercepts	s.e.	Slope	s.e.	Estimate intercepts	s.e.
N_0K_1C	−0.001527	0.000139	361.91	2.68	−0.002836	0.000494	350.24	3.18
N_2K_1C	−0.001527	0.000139	361.93	2.14	−0.000347	0.000756	321.03	5.90
N_3K_0	−0.001527	0.000139	363.86	2.16	−0.002332	0.000691	341.93	5.38
N_3K_1C	−0.001527	0.000139	367.20	2.14	−0.001137	0.000707	328.14	5.80
N_5K_1C	−0.001527	0.000139	367.97	2.16	−0.002546	0.000794	344.58	6.65
N_3K_1S	−0.001527	0.000139	367.97	2.19	−0.001078	0.000694	328.92	5.38
*All treatments	−0.001459	0.000136	364.30	2.46				

s.e. standard error.

* As treatments and blocking are not significant, simple linear regression can be applied.

Table 7
Ash composition of Miscanthus leaves (1st sampling), stems (1st sampling) and whole crop (4th sampling) for the third year crop from Treatment 2 (N_2K_1C).

	SiO_2	K_2O	CaO	MgO	P_2O_5	SO_3	Na_2O	Al_2O_3	Fe_2O_3	Mn_3O_4
Leaves 1st sampling	44.5	17.6	17.7	8.3	3.6	4.5	0.2	0.2	0.2	0.1
Stems 1st Sampling	26.4	50.4	4.7	7.3	4.2	4.6	0.4	0.3	0.1	0.1
Whole crop 4th Sampling	40.0	42.0	7.9	8.0	0.03	5.8	0.6	0.4	0.4	0.002

all treatments over the sampling period. This results in a wider range of metal contents in leaves and so the impacts on volatile combustion peak temperatures are more uniform and more significant than in stems. It can also be speculated that these differences could be associated with the form of the element in different parts of biomass, and that there is a synergy with other elements (e.g. between K and P), or the plant elements within the biomass biopolymers. In addition, differences in hemicellulose, cellulose and lignin concentrations between leaves and stems could have influenced these results. Different agronomy treatments result in different cell wall compositions, although these differences have been found to be very small in Miscanthus [25].

The impact of metals on char combustion peak temperature was found to be less significant than on volatile combustion peak temperature (data not shown). How catalytic metals impact on char combustion peak temperature is not yet fully established, since certain metals partition between volatiles and chars during combustion. Information, such as K remaining in the char and its form is still lacking. Hence, more work is needed to investigate the influence of metals in char combustion.

4. Conclusions

A comprehensive study of *Miscanthus x giganteus* agronomy in the UK has been carried out through the UK's Supergen Bioenergy Consortium activities. Six different fertiliser treatments over two growth years (270 samples in total) were chosen for this study, providing a solid foundation to more accurately evaluate Miscanthus combustion properties. Appropriate statistical analysis methods and analytical software (GenStat® 2009 Twelfth Edition, VCN International Ltd.) were applied to assess whether the differences between treatment and sampling time are valid. The following conclusions summarises the results from the agronomy treatment of Miscanthus, regarding fuel quality based on their C, N, K, Cl, S, and ash contents, calculated CV values and fouling indices, and combustion properties.

- Overall, Miscanthus stems have better fuel quality than leaves, as evidenced by their much lower ash, N and S contents, and slightly higher C contents (hence higher CVs).
- Regarding the agronomy treatments, increasing N in the fertiliser results in higher N and ash contents in the resultant fuels. Therefore the treatment without any N added into the fertiliser seems to result in a fuel of better quality – with lower N and ash content, but slightly higher C contents, and lower fouling indices. The treatment without any KCl in the fertiliser produced very similar results to the treatment without N added into fertiliser.
- In general, the late harvested Miscanthus samples have improved fuel quality, with lower N, Cl, ash contents, alkali index and slightly higher C contents. However, with the exception of the treatment without additional N added into the fertiliser, all other treatments yielded crops with ash compositions that fell within the 'fouling possible' to 'fouling certain to occur' predictions. These results suggest that fouling could be an issue for Miscanthus when additional N is used in the fertiliser in

order to improve yield. Fuel pre-treatment and boiler system changes may be needed to avoid ash related problems during Miscanthus combustion.
- Simple linear regression within groups (treatments) of data in GenStat is a useful tool to distinguish different patterns of response in the Miscanthus treatment trial. Correlations show relationships between the total metal content of leaves and stems with decreasing volatile combustion peak temperature (from TGA). Over the sampling period, the volatile combustion peak temperature increases as the total metals decrease. All linear regression models presented in this work show strong relationships between metal contents in different parts of Miscanthus and volatile combustion peak temperatures.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2013.09.003.

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