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The potential for production of high quality bio-coal from early harvested *Miscanthus* by hydrothermal carbonisation

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ABSTRACT

To meet combustion quality requirements, *Miscanthus* is conventionally harvested in late winter/early spring after senescence due to a lowering of fuel nitrogen, chlorine and ash content. This can overcome combustion issues such as slagging, fouling and corrosion however there is a significant reduction in dry matter yields compared to early harvesting in the autumn. In this study, *Miscanthus* × *giganteus* harvested conventionally (after senescence) and early (green) have been pre-treated by hydrothermal carbonisation (HTC) at 200 °C and 250 °C. HTC at 200 °C improves the grindability of the biomass but results in limited energy densification. HTC at 250 °C results in increased energy densification producing a bio-coal with a HHV ranging from 27 to 28 MJ/kg for early and 25 to 26 MJ/kg for conventional harvesting; the Hardgrove Grindability Index (HGI) increases from 0 to 150. At higher HTC temperatures, the combustion profile of the bio-coal exhibits a 'coal like' single stage combustion profile. HTC results in a significant reduction in alkali metal content, increases safe combustion temperatures and reduces the theoretical propensity of the derived fuel to slag, foul and corrode. The results indicate that HTC can valorise both conventional and early harvested *Miscanthus* without producing any adverse effect on the yields and quality of the bio-coal. The challenges associated with early harvesting of *Miscanthus* appear to be largely overcome by HTC resulting in increased yields of up to 40% per hectare due to reduction in dry matter loss.

1. Introduction

Miscanthus is a perennial bio-energy crop which is currently being commercially utilised in both Europe and the US. *Miscanthus* is viewed favourably as an energy crop, as being a C4 perennial rhizomatous grass, it offers enhanced carbon fixation, high water use efficiency and a rhizome which can store key nutrients from growth to be utilised in early spring offering higher yields along with low fertiliser and pesticide requirements [1].

Current bio-energy applications for *Miscanthus* are largely focused on thermal conversion routes such as combustion, however such routes have feedstock quality requirements, with the fuel parameters set by the combustion system design. Some of the most important physical properties include moisture content, bulk density and resistance to milling. Important chemical properties include the elemental properties of the fuel, notably the carbon, hydrogen, nitrogen, oxygen, sulphur, chlorine and metal content of the feedstock. The carbon, hydrogen and oxygen influence the energy density and combustion characteristics of the fuel; the nitrogen content, in part, influences nitrogen oxide (NO_x) emissions and chlorine and sulphur along with metals, in particular potassium, sodium, calcium, phosphorous, magnesium and iron contribute to ash related problems such as slagging, fouling, corrosion and agglomeration [2].

For *Miscanthus* to best fit the combustion quality requirements, it is conventionally harvested during the late winter or early spring in the UK, after which the crop has fully senesced and nutrients have been remobilised into the rhizome. Harvesting at that time tends to result in a fuel with a reduced above ground crop moisture content compared to that harvested at the peak of the growing season [3]. Also, the combined effect of leaf loss and nutrient translocation leads to a reduction in alkali metal content in the biomass in spring [4]: with Kahle et al., [5] reporting that the nitrogen, phosphorous and potassium content of the crop harvested late was 61%, 64% and 55% respectively of that harvested in the autumn.

While the winter/late harvesting of *Miscanthus* may increase thermal feedstock quality, late harvesting has an impact on net biomass yield. Typically, the maximum biomass yield occurs in the early autumn months just prior to senescence [4]. After this, and then during the

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winter, as the crop dries out, the breakage of leaves and stems result in an estimated decline in dry matter yield of 27 kg ha^{-1} day^{-1} [6] reaching an estimated total 30% decline of peak dry matter yield by the conventional harvesting time, which would represent a 43% increase in yield working back [7–9]. Moreover while late harvested *Miscanthus* samples have improved fuel quality, with lower nitrogen, chlorine, ash and alkaline metal content, the results presented in Baxter et al., [2] indicate that slagging, fouling and corrosion is still most probable in most crops. Thus, the reduction in nutrients brought about by overwintering is still insufficient to lead to safe combustion and also leads to a significant decrease in dry yield. Delaying harvest until after senescence does have the advantage that the crop can remobilise key plant nutrients such as nitrogen into the rhizome for regrowth in the spring and return some P and K to the soil through leaf fall [10,11] The longer term impact of continuous autumn harvesting is currently unknown, and there are concerns that earlier harvesting will prematurely exhaust the crop [9]. A number of studies have examined the impact of early harvesting on *Miscanthus* dry matter (DM) yields [4,12,13]. From these, there is some evidence that nitrogen management can play a role in ensuring sustainability of early cutting [4,13]. In the scientific literature, two studies have demonstrated early harvesting of *Miscanthus* × *giganteus* can be performed for three to four consecutive years without seeing a noticeable drop in yield [4,12]. One study identified a notable loss in yield in sites lacking nitrogen application [4]. A two-year study in Germany also found that *Miscanthus* × *giganteus* could tolerate early cutting [13], however without additional nitrogen, the yields were approximately half that of fertilised plots. In this case, the benefits of sustained yields must be offset though the moderate application of inorganic fertiliser [8]. Logistics of harvesting green crops should be similar to overwintered crops, with both crops harvested with forage harvesters. High moisture crops can pose storage difficulties due to microbial degradation and losses due to liquid effluent production and these factors would require further investigation [14].

Whether *Miscanthus* is harvested 'green' in the autumn or later after winter, a biomass pre-treatment which improves the fuels ash chemistry appears to be a pre-requisite for safe combustion and an autumn/green harvest will potentially achieve the highest possible yield per hectare. Hydrothermal carbonisation (HTC) is an emerging pre-processing technology for upgrading the physical and chemical properties of biomass before further conversion or combustion. HTC involves submerging biomass in water and heating to between 180 and 260 °C while maintaining pressures high enough to keep the water in a liquid phase. Under these conditions, the physical properties of water change, and promote a natural coal formation process, converting the biomass into bio-coal or hydrochar exhibiting similar properties to that of a low rank coal. Comprehensive reviews of HTC can be found in Libra et al., [15] and Kambo and Dutta [16].

During the HTC process, the modified aqueous conditions provide both the reagent and medium for a complex series of reactions which involve removal of hydroxyl groups through dehydration, removal of carboxyl and carbonyl groups though decarboxylation; and cleavage of many ester and ether bonds through hydrolysis. This result in a fuel which is: (i) more energy dense, through the removal of oxygen and hydrogen; (ii) easily friable due to the removal of colloidal structures; and (iii) more hydrophobic through a reduction in the hydrophilic functional groups [17].

Recent studies by Reza et al. [18] and Smith et al. [19] have reported of the fate of inorganics and heteroatoms during HTC of *Miscanthus* and indicate significant removal of the alkali metals, potassium and sodium, along with chlorine. A more limited removal of magnesium, calcium and phosphorus is observed and the net extraction largely governed by reaction temperature. Analysis of ash melting behaviour in Smith et al., [19] showed a significant reduction in the slagging propensity of the resulting fuel, along with the fouling and corrosion risk combined. This is accompanied by a doubling in the higher heating value, from 16.1 MJ/kg to 32.1 MJ/kg. Consequently HTC offers the potential to upgrade *Miscanthus* from a reasonably low value fuel into a high grade fuel, with a high calorific value, improved handling properties and favourable ash chemistry. Moreover, recovery of the extracted alkali and alkaline earth metals along with phosphorous and nitrogen (in the form of ammonium) from the process waters may allow the recovery of nutrients [20,21].

This investigation sets out to investigate the feasibility of using HTC to overcome the combustion limitations imposed by the inorganic chemistry of green/early harvested *Miscanthus*, with the aim to understand the influence of harvesting on the production of a high quality solid fuel for combustion.

2. Methodology

2.1. Materials

Samples of *Miscanthus* × *giganteus* were obtained from Rothamsted Research (co-ordinates 51.801851, −0.366692 North). The crop used in this study is a naturally occurring triploid hybrid of diploid *M. sinensis* and a tetraploid *M. sacchariflorus* [22]. In autumn 2015 the crop was 22 years old. The site has a silty clay loam soil with flints [23]. It was grassland for the majority of the previous 100 years and an adjacent *Miscanthus* crop had not responded (in terms of yield) to nitrogen fertiliser [24]. Therefore no nitrogen or other fertilisers were applied.

For this experiment the crop was harvested on the 24th November 2015 just after the initial onset of senescence, with the winter/spring harvest collected 8th March 2016. The site had previously been harvested in March 2015 and had a recorded yield of 14.4 t DM/ha. This was the first time the crop had been cut in autumn.

For this investigation, approximately 10 kg of crop was sampled from random whole canes in both harvesting periods and shipped directly to the site of analysis. Upon receipt, the samples were split into a whole crop (leaves and stems), leaves only and stems only. Samples were then cut and homogenised in a garden shredder to a particle size of approximately 5 mm in diameter. The moisture content of the *Miscanthus* was calculated using a moisture oven following the procedure set out in BS ISO 11722:2013. The samples were further split using a riffle box with one half processed as received and the other half oven dried at 60 °C for 72 h. For analytical purposes samples were further ground and homogenised to below 100 µm in a cryomill (Retsch, Germany).

2.2. Hydrothermal carbonisation

HTC was performed in a modified 2000 ml high pressure stainless steel batch reactor (Parr, USA) at 200 °C and 250 °C using removable quartz liners. The temperature of the reactor was controlled by a thermocouple located on the reactor inner wall and a PID controller. A second thermocouple was located in the centre of the reactor and these values taken as reaction temperature. Pressure and temperature were continually logged throughout the experiment. For each run a 10% solids loading (dry basis) was used with a combined mass of 1000 g per run. HTC runs were performed on as received samples and oven dried samples, with the moisture content pre-determined and the biomass and deionised water corrected accordingly. The experiments were designed to ensure that each run contained an equivalent of 100 g of dry biomass. The quartz liner, mass of biomass and mass of water was weighed before loading the reactor. Once sealed the reactor was evacuated using a vacuum pump to remove air and then flushed with argon twice before being pre-pressurised in argon to 5 bar. The reactor was then heated to the desired temperature at approximately 5 °C min^{-1} and the reaction temperature held for one hour at its isobaric pressures of 16 bar and 40 bar respectfully. After one hour, the reactor was removed from the heating jacket and allowed to air cool to room temperature. When cooled, the reactor pressure was noted along with the corresponding temperature before being depressurised into a gas sampling bag for analysis. Once opened, the quartz liner and contents was reweighed and any additional moisture on the reactor quantified using pre-weighed tissue paper. The solid and liquid products were separated by filtration under vacuum using 110 mm qualitative circles (Grade 3, Whatman, UK). The remaining solid sample in the quartz liner was recovered though repeated rinsing of the liner with the process water until the liner was clear of char. The process water yield was subsequently calculated by subtracting the starting mass of the liner and the wet hydrochar from the post-run mass of quartz liner and contents. The hydrochar was allowed to air dry in a ventilated fume cupboard for a minimum of 48 h, to gauge air dry moisture loss, and then oven dried at 60 °C overnight.

2.3. Analysis

2.3.1. Inorganic analysis

For analytical purposes, dried samples were further ground and homogenised to below 100 µm in a cryomill (Retsch, Germany). Inorganic elemental composition was determined by two methods; wavelength dispersive X-ray fluorescence (WD-XRF) and Atomic Absorption Spectroscopy (AAS). For XRF analysis, samples were ashed at 550 °C overnight in a muffle furnace to determine ash content in accordance with BS EN ISO 18122:2015 and then heated to 900 °C to convert any sulphates in the ash to oxides to avoid interaction with platinum. Approximately 0.7 g of ash was accurately weighed into a platinum crucible and made up to 7 g using lithium borates flux (SPEX, USA). The mixture was then heated to 1100 °C and cast in a platinum fusion disk mould using an automated fusion system (Katanax, Canada). The elemental composition of the ash was then determined by XRF (Rigaku, USA). Due to the high temperatures required for glass fusion; potassium, sodium, calcium, magnesium were determined by AAS as the alkali metals are known to volatilise below 900 °C thus XRF may underestimate their concentration, as specified in PD ISO/TS 16996:2015. For AAS analysis, 0.4 g of sample was digested in 10 ml hydrofluoric acid using polypropylene beakers and a steam bath to remove any silica. The residue was taken to dryness to remove residual hydrofluoric acid before being re-digested in 10 ml hydrochloric acid and transferred to a Pyrex beaker and heated to dryness on a hotplate to remove any residual fluorine. Residual organic material was then removed using a combination of nitric and sulphuric acid on a hotplate before being made up to volume in a volumetric flask and determined by AAS (Valiant, USA). The AAS was calibrated using standard elemental stock solutions (Spectrosol, UK) and two certified biomass reference materials (Elemental Microanalysis, UK) were used to check the calibration and extraction efficiency.

Chlorine and sulphur content was determined by combusting 0.2 g of sample in an oxygen bomb (Parr, USA) with 10 ml of distilled water as an aqueous absorption media. Post combustion a 24 V DC current was then passed though the bomb to dissipate phosphoric acid vapour, the bomb rinsed with deionised water and made up to a known volume. The chlorine and sulphur content was then calculated via ion exchange chromatography (Dionex, USA) of the bomb washings in accordance with ISO 16994:2016.

2.3.2. Organic analysis, combustion properties and ash measurement

Carbon, hydrogen, nitrogen, and oxygen content of the raw biomass and hydrochar was analysed using a Flash 2000 CHNS-0 analyser (Thermo Scientific, USA). The instrument was calibrated and checked using calibration standards and certified biomass reference materials (Elemental Microanalysis, UK). Figures are given on a dry free basis, with hydrogen and oxygen values corrected to account for residual moisture in accordance with ASTM D3180-15. The calorific values of the samples were calculated by Dulong's equation (see equation one). The residual moisture within the biomass was determined using a moisture oven (Carbolite, UK) at 105 °C under nitrogen in accordance with BS EN ISO 18134-2:2015 and the ash content determined at 550 °C using the methodology described in BS EN ISO 18122:2015. The volatile fraction, fixed carbon and ash content calculated using a thermogravimetric analyser (TGA) (Mettler Toledo, Switzerland) by heating 10 µg of homogenised sample to 900 °C at a rate of 25 °C min^{-1} in nitrogen, with holds at 105 °C and 900 °C before switching to air. Burning profiles, ignition, flame stability and burnout temperature were obtained by temperature programmed oxidation, heating 10 µg of homogenised sample to 900 °C in a TGA (Mettler Toledo, Switzerland) at a rate of 10 °C min^{-1} in air and calculating the weight loss and first derivative.

$$\text{HHV} = (0.3383*\%\text{Carbon}) + (1.422*\%\text{Hydrogen}) - (\%\text{Oxygen}/8) \tag{1}$$

2.3.3. Ash fusion testing

Ash fusion testing (AFT) was performed using a Carbolite digital ash fusion furnace. A digital camera is fixed to the front of the furnace to capture images of the illuminated ash while it is heated from 550 °C to 1570 °C at 7 °C min^{-1}. The tests were conducted in an oxidising atmosphere with an air flow of 50 ml min^{-1}. Cylindrical test pieces were formed using dextrin binder (Sigma-Aldrich, USA) and were run in duplicate. Photographs were taken at 5 °C intervals but as the test was performed in accordance with the standard method for the determination of ash melting behaviour (DD CEN/TS 15370-1:2006) stages were given to the nearest 10 °C. The key stage temperatures are as follows: beginning of shrinkage (SST), sample deformation temperature (DT), hemisphere temperature (HT) and flow temperature (FT).

2.3.4. Predictive slagging and fouling indices

To predict the likelihood of fouling during combustion, various slagging and fouling indices have been derived based on the mean chemical composition of the fuels. The equations for alkali index (AI), bed agglomeration index (BAI), and acid base ratio (R $\frac{b}{a}$), are given as Eqs. (2)–(4) in Table 1. For the AI an AI < 0.17 represents safe combustion, an AI $> 0.17 < 0.34$ predicts probable slagging and fouling and an AI > 0.34 predicts almost certain slagging and fouling [25]. For BAI, a value of BAI < 0.15 predicts that bed agglomeration is likely to occur [26]. For the R $\frac{b}{a}$ a value of < 0.5 indicates a low risk of slagging and an R $\frac{b}{a} > 1.0$ predicts a high to severe risk of slagging during biomass combustion.

Table 1
Predictive slagging and fouling indices.

Slagging/fouling index	Expression	Limit	
Alkali Index	$AI = \frac{Kg(K_2O + Na_2O)}{GJ}$	AI < 0.17 safe combustion AI $> 0.17 < 0.34$ probable slagging and fouling AI > 0.34 almost certain slagging and fouling	Eq. (2)
Bed Agglomeration Index	$BAI = \frac{\%\,(Fe_2O_3)}{\%\,(K_2O + Na_2O)}$	BAI < 0.15 bed agglomeration likely	Eq. (3)
Acid Base Ratio	$R\frac{b}{a} = \frac{\%\,(Fe_2O_3 + CaO + MgO + K_2O + Na_2O)}{\%\,(SiO_2 + TiO_2 + Al_2O_3)}$	R $\frac{b}{a} < 0.5$ low slagging risk	Eq. (4)

2.3.5. Resistance to milling

Resistance to milling was calculated using the Hardgrove Grindability Index (HGI), a scale used to assess a fuels resistance to grinding and thus the energy requirement to pulverise a fuel to the required 70% below 75 µm needed for pulverised coal applications. The HGI tries to mimic the behaviour of a fuel in a commercial ball and track type coal pulveriser manufactured by Babcock and Wilcox; as the fuel increases on the HGI scale, the energy requirement decreases [27]. The HGI tests were carried out using a calibrated 50 cm^3 ball mill (Retsch, Germany), using four HGI reference coals (ACIRS, Australia) with HGI of 26, 49, 69 and 94 and a line of best fit calculated using least squares. Due to differences in density between coals, bio-coals and feedstock, a volumetric HGI test was undertaken as recommended in Bridgeman et al., [28]. Samples were sieved for analysis to between 1.18 mm and 600 µm and 10 cm^3 accurately weighted to ± 0.0001 g. Samples were ground in a ball mill for 30 s at 15 Hz and then passed through a 75 µm sieve with the mass of the two fractions taken. Samples were analysed in triplicate.

3. Results and discussion

3.1. Influence of HTC on the bio-coal organic composition

Table 2 shows the ultimate analysis results for both homogenised whole plants, key plant components and their corresponding hydrochars, Table 3 contains the mass yields, calorific values and proximate analysis for both homogenised whole plants, key plant components and their corresponding hydrochars. The results show a significant increase in carbon density for the 250 °C treatments, with the 250 °C bio-coals typically having around 70 wt% carbon. The hydrothermally treated leaves have slightly lower carbon densities due to the higher ash content. This increasing carbon density corresponds to an increase in the fuels energy density, with the HHV of the resulting bio-coal increasing from 18 MJ/kg (db) to 27 MJ/kg (db) for early and 18 MJ/kg (db) to 25 MJ/kg conventionally harvested *Miscanthus* processed at 250 °C. The HHV (gross calorific value) for the 'as received samples' were slightly higher at 28 MJ/kg for early and 26 MJ/kg conventionally harvested *Miscanthus.* This would suggest a higher energy density fuel for the early harvested *Miscanthus*. Lower Heating Values (LHV) (net calorific value) have also been calculated for the fuels with the latter value taking into account the latent heat requirements for the water generated from the fuel bound hydrogen on a dry basis and, the water within the fuel and fuel bound hydrogen on an as received basis. Given in many combustion applications (e.g. coal power station) the latent heat is not recovered, LHV is often the more significant value, as it represents the overall energy available. The moisture contents given for the hydrochar in Table 3 are based on the moisture content after 48 h of air drying. The moisture for the whole untreated *Miscanthus* is the moisture as received at the laboratory and the moisture for the unprocessed leaf and stems is post oven drying at 60 °C overnight. The LHV of the unprocessed green harvested autumn *Miscanthus* is 5 MJ/kg (a.r.); principally due to the 57.7% moisture on harvesting. The same fuel, hydrothermally treated at 250 °C had a LHV of 26 MJ/kg (a.r.) after 48 h air drying.

The energy densification of the 250 °C bio-coals appear to be a result of changes to the ratio of carbon and oxygen (O/C) in the fuel, with the carbon content increasing, while the oxygen and ash content decreases. The Van Krevelen diagram shown in Fig. 1 illustrates how the O/C and hydrogen to carbon (H/C) ratios of the bio-coals compare with coals and lignin [29]. The results show that the 250 °C bio-coals have a more 'coal like' properties, with the O/C ratio predicting properties between lignite and bituminous coal, using coal data reported in Hatcher et al., [30]. The O/C ratios for the 250 °C bio-coals are fairly consistent for both early harvested and conventionally harvested crops, with the H/C ratios varying more between the two harvests. The early harvested *Miscanthus*, processed at 250 °C, has a higher H/C ratio than the conventionally harvested *Miscanthus* processed at the same temperature. This variation is likely due to changes in the composition of the feedstock, with the early harvested *Miscanthus* containing a higher proportion of leaf matter than when conventionally harvested. The results have shown that hydrothermally processing leaves at 250 °C results in a higher H/C ratio, than processing stems of the whole sample. This change could be due to differences in biochemical composition, with the leaf matter containing a higher proportion of hemi-cellulose [31], thus increasing the amount of hemi-cellulose within the feedstock and altering the hydrothermal process chemistry. The leaf matter is also associated with a higher inorganic content, containing a greater concentration of alkali metals, alkaline earth metals and silicon (see Table 4), with studies suggesting these metals have a catalytic influence bringing about higher H/C ratios [32].

The 200 °C treatments result in more limited energy densification (with HHV of 18.2 MJ/kg to 19.5 MJ/kg and 15.2 MJ/kg to 17.9 MJ/kg), without noteworthy increases in carbon density and reductions in oxygen density. The reduction in mass of approximately 25–30%

Table 2
Elemental composition for both homogenised whole plants, key plant components and their corresponding hydrochars.

		% Dry Basis					
		N (wt%)	C (wt%)	H (wt%)	S (wt%)	O (wt%)	Ash (wt%)
Whole Plant – Oven Dried Prior to Treatment	Autumn Whole Plant Raw	0.7 ± 0.0	52.2 ± 0.5	5.2 ± 0.1	0.1 ± 0.0	38.7 ± 0.4	3.1 ± 0.0
	Spring Whole Plant Raw	1.4 ± 0.2	46.2 ± 0.2	5.3 ± 0.3	0.1 ± 0.0	44.9 ± 1.4	2.1 ± 0.1
	Autumn Whole Plant HTC 200	1.0 ± 0.0	53.8 ± 0.2	5.6 ± 0.2	0.1 ± 0.0	43.1 ± 1.3	2.5 ± 0.1
	Spring Whole Plant HTC 200	0.9 ± 0.0	53.3 ± 0.0	4.8 ± 0.2	0.1 ± 0.0	39.3 ± 0.2	1.5 ± 0.1
	Autumn Whole Plant HTC 250	1.3 ± 0.0	69.7 ± 0.3	4.8 ± 0.2	0.1 ± 0.0	21.9 ± 0.1	2.2 ± 0.0
	Spring Whole Plant HTC 250	0.9 ± 0.0	70.7 ± 0.4	3.5 ± 0.6	0.1 ± 0.0	23.2 ± 0.4	1.4 ± 0.0
Plant Components – Oven Dried Prior to Treatment	Autumn Miscanthus Stems Raw	0.6 ± 0.0	48.9 ± 0.0	4.7 ± 0.1	0.1 ± 0.0	42.7 ± 0.9	3.0 ± 0.1
	Spring Miscanthus Stems Raw	1.0 ± 0.1	48.3 ± 0.4	4.7 ± 0.4	0.1 ± 0.0	43.6 ± 0.1	2.3 ± 0.2
	Autumn Miscanthus Stems HTC 250	0.9 ± 0.0	70.9 ± 0.4	5.0 ± 0.0	0.1 ± 0.0	21.4 ± 0.1	1.7 ± 0.1
	Spring Miscanthus Stems HTC 250	0.9 ± 0.0	70.3 ± 0.1	4.5 ± 0.7	0.1 ± 0.0	23.0 ± 0.0	1.3 ± 0.1
	Autumn Miscanthus Leaves Raw	1.3 ± 0.1	48.6 ± 0.6	5.3 ± 0.7	0.1 ± 0.0	38.3 ± 1.5	6.4 ± 0.4
	Spring Miscanthus Leaves Raw	1.8 ± 0.0	47.7 ± 0.3	5.0 ± 0.4	0.1 ± 0.0	41.2 ± 0.1	4.1 ± 0.2
	Autumn Miscanthus Leaves HTC 250	1.5 ± 0.0	67.1 ± 0.6	6.5 ± 0.7	0.2 ± 0.0	18.0 ± 0.3	6.7 ± 0.2
	Spring Miscanthus Leaves HTC 250	1.7 ± 0.0	66.6 ± 0.3	5.5 ± 0.2	0.2 ± 0.0	21.1 ± 0.0	5.0 ± 0.1
Whole Plant – Treated as Received	Autumn Whole Plant HTC 200	0.6 ± 0.0	48.3 ± 0.3	5.3 ± 0.5	0.1 ± 0.0	43.1 ± 0.2	2.7 ± 0.1
	Spring Whole Plant HTC 200	0.8 ± 0.0	53.8 ± 1.1	4.8 ± 0.3	0.1 ± 0.0	33.4 ± 0.8	1.7 ± 0.1
	Autumn Whole Plant HTC 250	0.8 ± 0.1	72.3 ± 0.7	5.2 ± 0.1	0.1 ± 0.0	19.4 ± 0.7	2.2 ± 0.4
	Spring Whole Plant HTC 250	0.9 ± 0.1	70.3 ± 0.3	4.6 ± 0.4	0.1 ± 0.0	22.9 ± 0.3	1.4 ± 0.0

Table 3
Combustion and handling characteristics for both homogenised whole plants, key plant components and their corresponding hydrochars.

		Yield (wt%) (dry)	Moisture (wt%) (a.r.)	HHV (MJ/kg) (dry)	HHV (MJ/kg) (a.r.)	LHV (MJ/kg) (dry)	LHV (MJ/kg) (a.r.)	Volatile Matter (wt%) (dry)	Fixed Carbon (wt%) (dry)	HGI	slagging and fouling indices		
											AI	BAI	Rb/a
Whole Plant – Oven Dried Prior to Treatment	Autumn Whole Plant Raw	n.a.	57.7[a]	18.2	7.7	17.1	5.1	84 ± 0	12 ± 0	0 ± 0	0.31	0.02	0.90
	Spring Whole Plant Raw	n.a.	33.6[a]	15.2	10.1	14.0	8.1	83 ± 0	15 ± 0	0 ± 0	0.23	0.01	0.65
	Autumn Whole Plant HTC 200	76	4.4[b]	19.5	18.6	18.3	17.3	75 ± 0	20 ± 0	36 ± 3	0.09	0.02	0.43
	Spring Whole Plant HTC 200	71	8.0[b]	17.9	16.5	16.8	15.2	81 ± 0	17 ± 0	25 ± 0	0.11	0.03	0.29
	Autumn Whole Plant HTC 250	49	3.7[b]	26.5	25.5	25.4	24.4	59 ± 0	39 ± 0	142 ± 1	0.07	0.03	0.44
	Spring Whole Plant HTC 250	47	2.8[b]	24.8	24.1	24.0	23.3	42 ± 0	150 ± 2	150 ± 2	0.05	0.04	0.44
Plant Components – Oven Dried Prior to Treatment	Autumn *Miscanthus* Stems Raw	n.a.	7.7[c]	15.6	14.4	14.6	13.2	75 ± 0	22 ± 0	0 ± 0	0.34	0.01	0.87
	Spring *Miscanthus* Stems Raw	n.a.	7.1[c]	15.2	14.1	14.2	12.9	83 ± 0	14 ± 0	0 ± 0	0.19	0.01	0.61
	Autumn *Miscanthus* Stems HTC 250	49	4.3[b]	27.4	26.2	26.3	25.0	58 ± 0	41 ± 0	144 ± 1	0.06	0.13	0.51
	Spring *Miscanthus* Stems HTC 250	43	3.0[b]	26.1	25.3	25.1	24.2	56 ± 0	43 ± 0	145 ± 2	0.05	0.03	0.73
	Autumn *Miscanthus* Leaves Raw	n.a.	7.5[c]	17.2	15.9	16.0	14.6	83 ± 0	11 ± 0	1 ± 0	0.36	0.02	0.19
	Spring *Miscanthus* Leaves Raw	n.a.	7.1[c]	15.9	14.8	14.8	13.5	82 ± 0	14 ± 0	1 ± 0	0.55	0.01	0.71
	Autumn *Miscanthus* Leaves HTC 250	45	4.1[b]	28.8	27.6	27.4	26.1	62 ± 0	31 ± 0	139 ± 0	0.05	0.20	0.22
	Spring *Miscanthus* Leaves HTC 250	46	3.5[b]	26.6	25.7	25.4	24.4	58 ± 0	37 ± 0	144 ± 2	0.09	0.05	0.27
Whole Plant – Treated as Received	Autumn Whole Plant HTC 200	76	7.1[b]	16.2	15.0	15.0	13.7	85 ± 1	11 ± 1	34 ± 1	0.10	0.04	0.45
	Spring Whole Plant HTC 200	73	4.1[b]	19.1	18.3	18.0	17.2	85 ± 1	11 ± 3	25 ± 0	0.10	0.02	0.39
	Autumn Whole Plant HTC 250	48	4.0[b]	28.4	27.3	27.3	26.0	60 ± 1	38 ± 1	151 ± 1	0.05	0.04	0.41
	Spring Whole Plant HTC 250	49	3.0[b]	26.2	25.4	25.2	24.3	57 ± 1	42 ± 1	145 ± 2	0.05	0.03	0.46

n.a. not applicable.

[a] As received.

[b] Moisture 48 h after treatment.

[c] Oven dried at 60 °C.

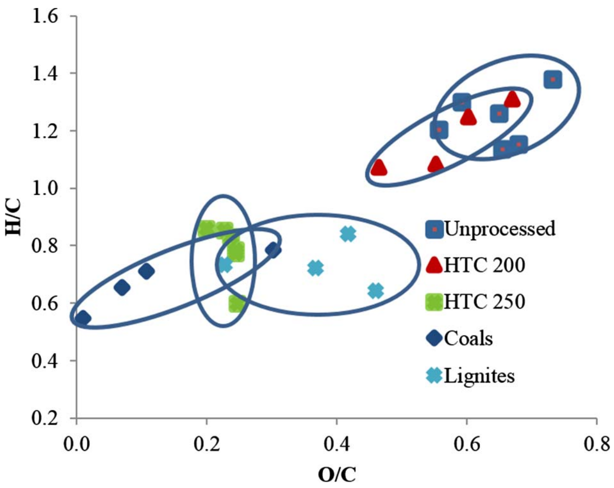

Fig. 1. Van Krevelen diagram showing the bio-coals, unprocessed biomass, mineral lignite and mineral coals (lignite and coals adapted from Hatcher et al. [27]).

suggests decomposition of some of the biochemical components at 200 °C without significant repolymerisation. This limited energy densification, on its own should however not dissuade from this treatment, for the removal of some of the biochemical components makes the fuel more grindable, with a substantial improvement in the fuels HGI which could lead to energy savings when grinding and improvements in flame stability if used in pulverised coal applications. Moreover when the 'as received' moisture content of the unprocessed *Miscanthus* is considered, the 200 °C treatments give significantly higher LHV and could avoid, or at least reduce the need for thermal drying. Treatment of the 'as received' feedstocks increased the LHV from 5 MJ/kg (a.r.) and 8 MJ/kg (a.r.) to 14 MJ/kg (a.r.) and 17 MJ/kg (a.r.) for the early and conventionally harvested *Miscanthus* respectively. This is principally due to the enhanced dewateribility of the bio-coal; due to its greater hydrophobicity [33].

Removal of the oxygen containing functional groups is advantageous as these can act as bonding sites for cations, such as sodium, potassium, magnesium, calcium, in biomass and lower-rank coals [34]. It has been suggested that HTC reduces the fouling risk though the combination of decreased oxygen and volatile matter content of the bio-coal [35]. Proximate analysis of the bio-coals in Table 3 shows that the volatile matter fraction is reduced from approximately 83% for both early and conventionally harvested *Miscanthus* to approximately 60% for the corresponding 250 °C treated bio-coals.

3.2. *Influence of HTC on the bio-coal combustion chemistry*

Application of biomass in pulverised coal-fired power plants is often favourable as it involves utilising existing infrastructure. Most of these pulverised coal-fired power plants have usually been built to burn a 'design' fuel, whereby the design fuel is usually a typical coal from the locality. These design fuels use parameters including ash content, HGI, volatile matter content, combustion behaviour, and slagging and fouling characteristics in an attempt to account for boiler performance [36]. Consequently for pulverised coal applications, fuel specifications are often site-specific and for pulverised fuel applications, where the design fuel becomes unavailable, different coals are typically blended to best match the performance parameters. Thermo-gravimetric analysis (TGA) is one method originally developed by Babcock and Wilcox for comparing and evaluating fuels and by calculating the first derivative thermogravimetric (DTG) curve, with four characteristic temperatures being typically interpreted [34]. The first initiation temperature occurs where the weight first begins to fall; the second initiation temperature occurs where the weight loss accelerates due to the onset of char (fixed carbon) combustion. The third is the peak temperature where the weight loss is maximum; and the fourth is the burn-out temperature where the weight is constant, indicating the completion of combustion [34].

Fig. 2 shows the DTG curves for unprocessed *Miscanthus*, processed at 200 °C, samples processed at 250 °C and a reference bituminous coal (Elemental Microanalysis B2306, batch 203830). Fig. 2a shows the burning profile of the unprocessed early and conventionally harvested *Miscanthus* and compares the profiles to a reference coal. The unprocessed biomass has a distinctive two peak profile at 300 °C and 440 °C respectfully, whereby the volatile material burns, peaking at 300 °C. The rate of loss then reduces before the char ignites and with a peak burn temperature at 440 °C. Coal on the other hand has almost a single stage whereby the volatile burn starts at the first initiation temperature, around 325 °C, with a 'shoulder' on the curve before the onset of char combustion at the second initiation temperature due to the onset of char combustion, around 460 °C, with peak temperature around 550 °C. The lower decomposition temperatures associated with many biomass fuels result in challenges in operation of the pulveriser mills and require lower temperatures compared to coal to avoid fuel decomposition. When burning fuel, it is important to achieve flame stability to sustain the flame and ensure safe boiler operation. To achieve a stable flame you first need to achieve ignition, whereby you attain substantial burning of a combustible material. To achieve ignition there is an initial heat loss due to the evaporation of any residual water and heating of the particle to the first initiation temperature (approximately 200 °C for conventionally harvested *Miscanthus*); this heat loss needs to be balanced by the heat release at the ignition temperature. Flame stability requires the rate of burning (flame velocity) to match the rate of material feed. If these are not matched, the flame will either blow off or flash back [36]. Differences in the nature different fuels burn (as shown by the burning profile) when co-fired can lead to poor burn interaction, with essentially the two fuels burning independently of each other resulting in challenges in maintaining flame velocity. The mismatched burning profiles of the coal and the unprocessed *Miscanthus* in Fig. 2a may lead to a poor burn interaction as ignition temperatures do not overlap bringing about challenges in maintaining flame velocity and flame stability.

Flame stability can be further exacerbated by differences in particle size as large particle sizes can act as heat sinks, increasing the resonance time of the particle before ignition and influencing the balance of heat loss and heat release. For a stable flame in a pulverised coal operation, pulverisation of fuel to 70% below 75 µm is typically required. The ease in which fuels can be pulverised to 70% below 75 µm is described using the Hardgrove Grindability Index (HGI). Coals typically lie between 30 (increased resistance to pulverization) and 100 (more easily pulverised) on the scale.

The HGI for the unprocessed *Miscanthus* and processed bio-coals are given in Table 3. The unprocessed *Miscanthus* has an HGI of zero which essentially implies under the test conditions, that no fuel would reach the desired 75 µm and thus, assuming co-milling, there would be either a greater energy requirement for milling to achieve 75 µm or the pulverised fuel particles would be greater than 75 µm in diameter. The lower first initiation temperature of the unprocessed *Miscanthus* would to a certain extent offset a larger particle diameter as heat loss due to the greater heat sink would be balanced by the earlier heat release. This would however only apply to a point after which the larger particles, on drying and de-volatilization, will became entrained in the gas stream and move higher in the furnace while still burning. This will promote flame instability [34].

Fig. 2f shows the combustion profiles of the conventionally harvested unprocessed *Miscanthus*, processed at 200 °C and 250 °C and the reference coal (Elemental Microanalysis B2306, batch 203830). The profiles show the influence of HTC treatment on the fuels combustion profiles. The samples processed at 200 °C retain the distinctive two peaks at 300 °C and 460 °C brought about by independent volatile and char burnout, similar to that of unprocessed *Miscanthus*. The 200 °C

Table 4
Fuel inorganic and heteroatom chemistry.

		PPM_{fuel} (db)										
		Na	K	Mg	Ca	Mn	Fe	Al	Si	P	S	Cl
Whole Plant – Oven Dried Prior to Treatment	Autumn Whole Plant Raw	660 ± 30	3970 ± 300	720 ± 100	2150 ± 200	80 ± < 5	70 ± < 5	80 ± < 5	5370 ± 50	410 ± 5	860 ± 30	4390 ± 80
	Spring Whole Plant Raw	520 ± 10	2360 ± 80	830 ± 120	2050 ± 250	10 ± < 5	30 ± < 5	40 ± < 5	5870 ± 140	440 ± 10	890 ± 80	6300 ± 270
	Autumn Whole Plant HTC 200	540 ± 30	1440 ± 20	590 ± 40	1670 ± 110	50 ± < 5	30 ± < 5	20 ± < 5	6660 ± 130	380 ± 20	750 ± 30	3440 ± 10
	Spring Whole Plant HTC 200	280 ± 40	1110 ± 20	450 ± 10	1000 ± 10	70 ± < 5	50 ± < 5	50 ± < 5	6940 ± 230	470 ± 10	590	2910
	Autumn Whole Plant HTC 250	360 ± 30	1090 ± 5	520 ± 0	1760 ± 100	70 ± < 5	40 ± < 5	30 ± < 5	5750 ± 70	720 ± 20	850 ± 30	1640 ± 50
	Spring Whole Plant HTC 250	320 ± 30	590 ± 70	370 ± 50	1040 ± 40	70 ± < 5	30 ± < 5	10 ± < 5	3670 ± 70	550 ± 10	960 ± 40	1640 ± 40
Plant Components – Oven Dried Prior to Treatment	Autumn *Miscanthus* Stems Raw	220 ± 10	4120 ± 40	810 ± 40	2030 ± 120	80 ± < 5	30 ± < 5	170 ± 10	5210 ± 80	490 ± 10	600 ± 20	4250 ± 80
	Spring *Miscanthus* Stems Raw	300 ± 10	2110 ± 30	810 ± 30	1430 ± 80	80 ± < 5	20 ± < 5	n/d	5060 ± 220	400 ± 10	830 ± 30	5560 ± 100
	Autumn *Miscanthus* Stems HTC 250	350 ± 80	940 ± 80	380 ± 20	1760 ± 100	60 ± < 5	140 ± 10	190 ± 10	4480 ± 130	680 ± 20	960 ± 40	2530 ± 60
	Spring *Miscanthus* Stems HTC 250	370 ± 30	620 ± 20	430 ± 5	1360 ± 40	50 ± < 5	20 ± < 5	n/d	2620 ± 100	400 ± 20	1030 ± 30	5040 ± 110
	Autumn *Miscanthus* Leaves Raw	1020 ± 80	3970 ± 30	720 ± 20	2150 ± 120	80 ± < 5	70 ± < 5	80 ± 5	27,330 ± 800	410 ± 20	900 ± 30	5830 ± 100
	Spring *Miscanthus* Leaves Raw	680 ± 30	6470 ± 80	1150 ± 20	3390 ± 240	130 ± < 5	50 ± < 5	50 ± 5	10,560 ± 260	630 ± 10	1250 ± 50	7030 ± 100
	Autumn *Miscanthus* Leaves HTC 250	290 ± 10	850 ± 70	550 ± 20	6940 ± 100	150 ± < 5	200 ± 10	240 ± 10	27,330 ± 410	1800 ± 20	1670 ± 30	2120 ± 40
	Spring *Miscanthus* Leaves HTC 250	280 ± 10	1790 ± 70	690 ± 5	2360 ± 100	160 ± < 5	100 ± 10	n/d	12,760 ± 130	2180 ± 30	1970 ± 80	1650 ± 60
Whole Plant – Treated as Received	Autumn Whole Plant HTC 200	220 ± 5	1050 ± 10	360 ± 10	1680 ± 20	50 ± < 5	50 ± < 5	100 ± 5	4870 ± 130	440 ± 20	760 ± 20	2740 ± 80
	Spring Whole Plant HTC 200	380 ± 40	1170 ± 20	470 ± 10	920 ± 10	50 ± < 5	30 ± < 5	n/d	5110 ± 90	262 ± 10	570 ± 20	3140 ± 200
	Autumn Whole Plant HTC 250	210 ± 20	960 ± 10	370 ± 20	1830 ± 30	60 ± < 5	50 ± 10	120 ± 20	5420 ± 150	674 ± 60	860 ± 20	2420 ± 40
	Spring Whole Plant HTC 250	420 ± 10	550 ± 30	360 ± 50	860 ± 40	60 ± < 5	30 ± < 5	< 10	3240 ± 60	40 ± 10	810 ± 80	1330 ± 100

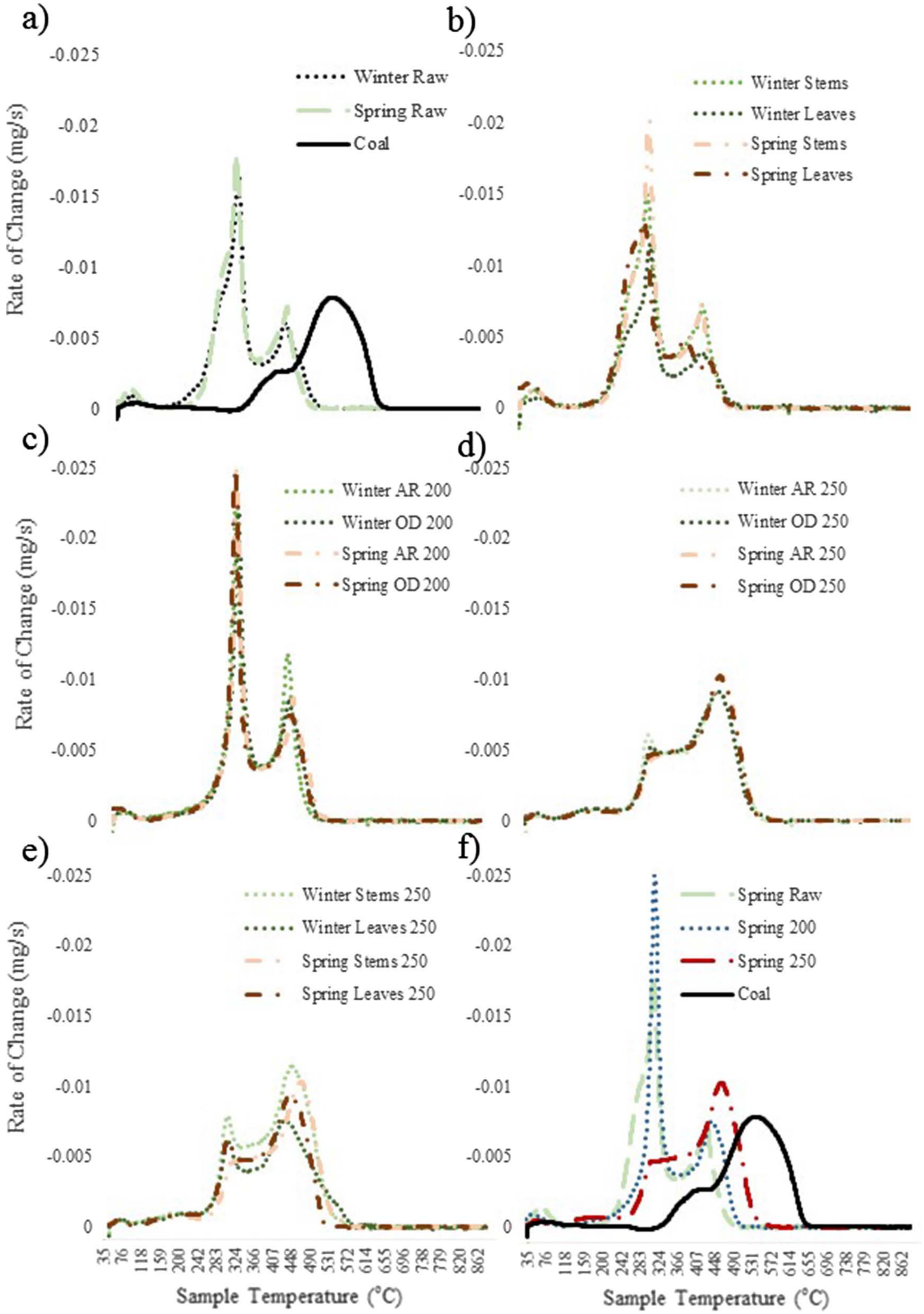

Fig. 2. Derivative thermogravimetric (DTG) burning profiles for: a) early and conventionally harvested unprocessed *Miscanthus* and bituminous reference coal (Elemental Microanalysis B2306, batch 203830); b) early and conventionally harvested unprocessed *Miscanthus* leaf and stem; c) early and conventionally harvested *Miscanthus* hydrothermally treated at 200 °C; d) early and conventionally harvested *Miscanthus* hydrothermally treated at 250 °C; e) early and conventionally harvested leaf and stem hydrothermally treated at 250 °C; and f) conventionally harvested *Miscanthus*, unprocessed, hydrothermally treated at 200 °C, hydrothermally treated at 250 °C and bituminous reference coal (Elemental Microanalysis B2306).

treated samples do however differ from the unprocessed samples, and exhibit a slightly higher initiation temperature, most likely due to the hydrolysis and removal of the hemi-cellulose from within the fuel [37]. There is also a greater rate of mass loss observed at 300 °C, due to an increased level of cellulose within the fuel. This may be beneficial and allow pulverising mills to be run at a higher temperature consistent with coal operation. The HGI of 25 (see Table 3) for the samples processed at 200 °C suggests that the fuel will pulverise, albeit like a high resistance coal. For reference, a change in HGI from 15 to 43 represents a 50% reduction in the energy requirement for milling, so going from an HGI of zero to 25 would represent a significant energy saving [27]. Bio-coal exhibiting a HGI of 25 would bring about a smaller particle size within the furnace, reducing issues with flame stability. Solid fuels exhibiting lower volatile ignition temperature, may not need the same amount of size reduction required for pulverised coal applications as heating of the particle to the volatile ignition temperature is lower. This allows for a larger particle diameter when compared to coal firing, so firing should be possible even if 70% of the 200 °C hydrothermally treated fuel mass fails to meet the 75 μm, as typically required in pulverised applications.

Fig. 2f also shows that the samples processed at 250 °C, adopts a ‘coal like’ single stage combustion profile, albeit with a lower first initiation temperature at 270 °C compared with 325 °C, and a lower peak temperature around 480 °C as opposed to 550 °C for the bituminous reference coal. The volatile burnout is also more pronounced for *Miscanthus* processed at 250 °C than for the bituminous coal due to the higher volatile matter content of the bio-coal. The higher volatile matter content of the bio-coal can nevertheless be beneficial as this, along with the lower initiation temperature, will promote early ignition of the total fuel mass when co-fired; leading to better and more complete combustion. This early ignition in turn can also be beneficial for nitrogen oxide emissions as it will consume additional oxygen, increasing the fuel staging effects of low-NOx burners [34]. The HGI of 150 (see Table 3) for the samples processed at 250 °C also imply that the fuel will easily pulverise and there should be limited issues with flame stability brought about though larger particle diameters encountered with untreated biomass.

Fig. 2b shows the burning profiles of the unprocessed leaf and stem components. The burning profiles show differences between the stem and the leaf depending on the time of harvest, principally due to senescence and weathering degrading the plant biochemical components and removing inorganics, changing the ash content. These differences in composition also influence the burning profile of the bio-coal as shown in Fig. 2e. The autumn stems, the autumn leaves and spring leaves both exhibit a distinct volatile peak, which may suggest the presence of residual cellulose or increased reactivity of the volatiles. This may account for the higher energy densities seen in the early harvested samples. For the conventionally harvested stems treated at 250 °C, a coal like single stage combustion profile is observed whereby the transition between the volatile release and initiation of char burn (second initiation temperature) is marked more by a ‘shoulder’ as opposed to a distinct peak. This happens despite only a modest reduction in volatile matter (Table 3). The autumn components also appear more reactive than the conventionally harvested components with reduced peak temperature in the char burnout. This is most likely due to the higher potassium content (see Table 4) catalysing the volatile burn [38].

The two stage combustion profile described for the early harvested 250 °C plant component samples is also retained in the homogenised early harvest samples when compared with the conventionally harvested samples in Fig. 2d. The 250 °C conventionally harvested samples displaying the single stage combustion profile similar to the conventionally harvested stems treated at 250 °C. This change is brought about though a modest reduction in volatile matter content (Table 3), which brings about a slight change in the overall profile. Table 4 gives the inorganic content of the fuel, with the potassium content higher in the autumn samples. Higher potassium content is known to catalyse the volatile burn and could explain these differences [38] but the biochemical composition of the starting feedstock will be slightly different due to the higher proportion of leaf matter in the early harvested feedstock and needs to be also considered. Both these factors will influence the combustion profiles for the two unprocessed feedstock in Fig. 2a. Fig. 2c shows the early and conventionally harvested *Miscanthus* treated at 250 °C and shows increased reactivity of the char burn in the autumn samples. The HGI appears reasonably constant for both the 200 °C and 250 °C treatments whether treating autumn or spring feedstock.

3.3. Influence of HTC on the inorganic chemistry

Inorganics can be a particular issue for *Miscanthus* during combustion as large amounts of alkali and alkaline metals, particularly potassium and sodium, along with sulphur and chlorine influence ash chemistry and influence the behaviours of the fuel in terms of its tendency to corrode equipment and cause slagging, fouling and in certain furnaces bed agglomeration [39]. Slagging is a phenomenon brought about though the melting of ash when ash deposits are exposed to radiant heat, such as flames in a furnace. As most furnaces are designed to remove ash as a powdery residue, having a high ash melting temperature is often desirable. Otherwise it has a higher tendency to fuse into a hard glassy slag, known as a clinker, which can be difficult to remove from the furnace [39]. The temperature at which the ash melts and fuses is strongly influenced by the alkali and alkaline metals which act as a flux for alumina-silicate ash. Potassium and sodium generally reduce the ash melting temperature, while magnesium and calcium generally increase it [39]. The AFT is a qualitative method of assessing the propensity of a fuel to slag and works by heating an ash test piece and analysing the transitions in the ash chemistry. Key transitions include; (i) shrinkage, which predominantly represents the decomposition of carbonates in hydrothermally derived chars, (ii) deformation temperature, essentially representing the onset point at which the powdery ash starts to agglomerate and starts to stick to surfaces, (iii) hemisphere, whereby ash is agglomerating and is sticky and (v) flow, whereby the ash melts. For most power stations, slagging becomes problematic between the deformation and hemisphere temperature. Fig. 3 displays the deformation, hemisphere and flow temperatures for the autumn and spring whole plant unprocessed and treated at 200 °C and 250 °C. The safe combustion temperature is taken as the deformation temperature in Fig. 3. Table 5 state the transition temperatures for all samples along with their standard errors.

The results show that the unprocessed early harvested *Miscanthus* behaves the most poorly in the AFT with the deformation temperature (i.e. safe combustion temperature) of only 1040 °C. The conventionally harvested *Miscanthus* behaves better with a deformation temperature around 1140 °C. The cause of this appears to be the higher potassium content within the fuel, relative to silicon content, in the unprocessed early harvested crop. Interpretation of this data requires some caution however as despite the early harvested *Miscanthus* having the lower deformation temperature and the higher potassium content, the conventionally harvested crop has 2000 ppm more chlorine. Given the release of potassium depends more on the chlorine content than the potassium content alone [40], the corrosion and fouling potential may be higher for the conventionally harvested *Miscanthus*, with retention of potassium in the ash arguably more favourable.

Hydrothermally treating the early harvested *Miscanthus* at 200 °C appears to reduce the potassium content from 4000 ppm to 1000 ppm and this increases the deformation temperature to 1150 °C, however there is only a minimal improvement with the conventionally harvested *Miscanthus* treated at 200 °C. This change is due to the reduction of potassium in the 200 °C treated samples being accompanied by reductions in fuel silicon and calcium. Calcium has been shown to increase the silicon fluxing temperature [41] and consequently its removal will

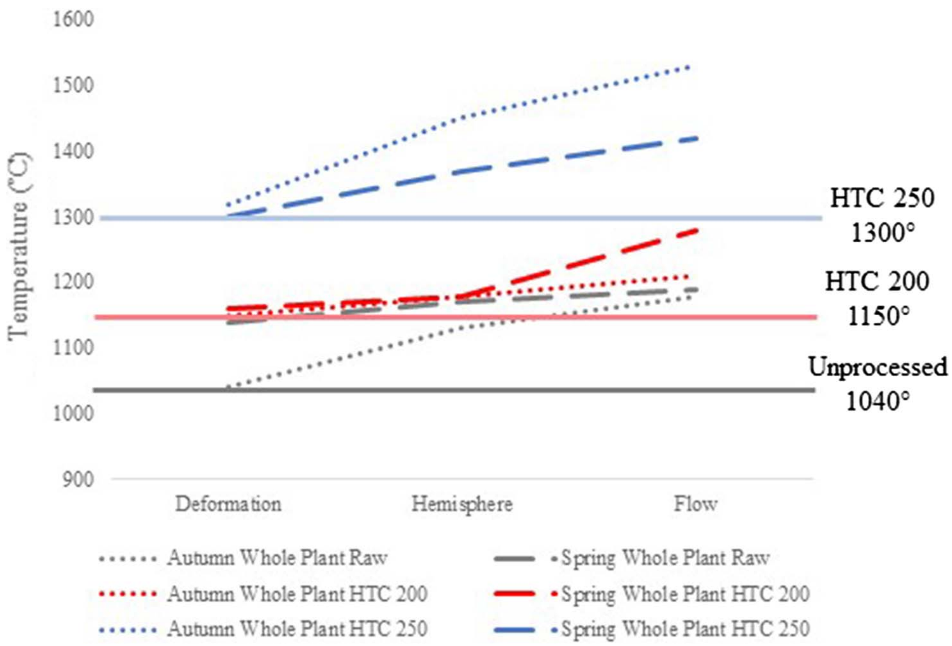

Fig. 3. Ash Fusion Temperatures for the whole plant, oven dried prior treatment.

reduce the melting temperature, while the reduction in potassium will lead to an increase in ash melting temperature. Consequently for the 200 °C treated samples, the change in the potassium to silicon ratio is less than the overall reduction in potassium due to corresponding reductions in silicon. The reduction of calcium will reduce the buffering offered by the calcium, which reduces the fluxing temperature of silicon due to potassium. Thus, despite the lower potassium content, the silicon melts at a similar temperature due to an overall reduction in silicon and calcium. It should however be noted that despite little change in deformation temperature, the overall ash content has reduced for both 200 °C treated samples; this in turn changes the fuels from one with probable slagging and fouling to one which can be safely combusted according to the alkali index (see Table 3).

The 250 °C treated samples exhibit a significant increase in transition temperature, with both the early and conventionally harvested *Miscanthus* increasing to 1320 °C and 1300 °C respectively, leading to a noteworthy increase in the safe combustion temperature. There is also a further increase in the hemisphere region with temperatures up to 1450 °C being observed (hemisphere temperature is reported as the upper limit for safe combustion by some authors). Of the early and conventionally harvested *Miscanthus* feedstocks, there appears to be a higher potassium content within the early harvested *Miscanthus* than conventional (approximately 1000 ppm and 600 ppm respectively) however the silicon content is also higher for the early harvested *Miscanthus* (approximately 5500 ppm and 3500 ppm respectively) and this appears to offset any fluxing brought about by the potassium. The early harvested *Miscanthus* also appears to contain a higher concentration of calcium and phosphorous, with the latter known to increase the thermal stability of potassium when present as potassium phosphate [42]. The highest ash thermal stability was observed for the hydrothermally related leaves, with the early harvested leaf deformation temperature exceeding the furnace limit at 1570 °C. This high thermal stability is exhibited due to the high silicon content within the leaves. Silicon is largely retained within the bio-coal while the high

Table 5
Ash fusion transition temperatures for both homogenised whole plants, key plant components and their corresponding hydrochars.

Sample		Onset Temperature (°C)			
		Shrinkage	Deformation	Hemisphere	Flow
Whole Plant – Oven Dried Prior to Treatment	Autumn Whole Plant Raw	930 ± 0	1040 ± 15	1130 ± 0	1180 ± 0
	Spring Whole Plant Raw	960 ± 0	1140 ± 5	1170 ± 0	1190 ± 0
	Autumn Whole Plant HTC 200	1020 ± 0	1150 ± 0	1180 ± 0	1210 ± 0
	Spring Whole Plant HTC 200	900 ± 0	1160 ± 0	1180 ± 0	1280 ± 5
	Autumn Whole Plant HTC 250	850 ± 0	1320 ± 0	1450 ± 5	1530 ± 0
	Spring Whole Plant HTC 250	930 ± 25	1300 ± 15	1370 ± 5	1420 ± 30
Plant Components – Oven Dried Prior to Treatment	Autumn *Miscanthus* Stems Raw	1050 ± 0	1180 ± 0	1190 ± 0	1200 ± 0
	Spring *Miscanthus* Stems Raw	990 ± 0	1110 ± 0	1140 ± 0	1190 ± 0
	Autumn *Miscanthus* Stems HTC 250	990 ± 0	1300 ± 0	1350 ± 0	1370 ± 0
	Spring *Miscanthus* Stems HTC 250	830 ± 0	1250 ± 0	1320 ± 0	1360 ± 5
	Autumn *Miscanthus* Leaves Raw	1050 ± 0	1180 ± 0	1190 ± 0	1200 ± 0
	Spring *Miscanthus* Leaves Raw	700 ± 0	950 ± 0	1020 ± 5	1120 ± 0
	Autumn *Miscanthus* Leaves HTC 250	1060 ± 0	> 1570		
	Spring *Miscanthus* Leaves HTC 250	880 ± 0	1390 ± 0	1530 ± 0	1570 ± 0
Whole Plant – Oven Dried Prior to Treatment	Autumn Whole Plant HTC 200	970 ± 5	1150 ± 5	1220 ± 5	1270 ± 5
	Spring Whole Plant HTC 200	990 ± 5	1140 ± 5	1200 ± 20	1230 ± 25
	Autumn Whole Plant HTC 250	850 ± 100	1320 ± 10	1450 ± 25	1530 ± 20
	Spring Whole Plant HTC 250	970 ± 70	1300 ± 0	1430 ± 0	1470 ± 60

potassium content of the leaves is largely extracted. This would suggest that harvesting the *Miscanthus* with an increased leaf content, as is done with early harvesting, does not adversely influence the ash chemistry, but potentially enhances it. The energy density of the hydrothermally treated leaves is not too dissimilar to the energy density of the stems (27.4 MJ/kg (db) to 28.3 MJ/kg (db)), and with similar HTC yields, the presence of leaves through early harvesting does not appear to have any adverse effect. In addition, the leaves will improve the acid base ratio due to increased silicon within the ash (see Table 3), while increasing the feedstock yield by up to 40% by avoiding overwinter dry matter loss [7,8].

Fouling is a phenomena brought about when potassium and sodium, in combination with chlorine, partially evaporate when exposed to radiant heat and form alkali chlorides which condense on cooler surfaces such as heat exchangers. These deposits don't just reduce heat exchanger efficiency; they also play a major role in corrosion as these deposits can react with sulphur in the flue gas to form alkali sulphates releasing chlorine. This chlorine has a catalytic effect which results in the active oxidation and corrosion of the furnace material [39,43]. The bio-coals have been shown to undergo significant reductions in alkaline metals, most notably potassium, on a mass basis and this is also associated with reductions in fuel chlorine (see Table 4). The feedstock is already low in sulphur, containing typically 0.1 wt% (db) with limited change in concentration through treatment (see Tables 1 and 4). The inorganic analysis suggests that corrosion, associated with fouling should be reduced following treatment by HTC.

Caution is however required here as the release of volatile and non volatile metals can be linked to the volatile content of the biomass. Baxter and co-workers demonstrated that volatile matter is important in transport and volatilisation of both volatile and non-volatile metals during combustion and thus affects a fuels propensity to foul. During the devolatilisation stage, functional groups containing oxygen, can transport associated cations, assisting the volatilisation of both volatile and non-volatile metals [44]. During the HTC process, alkali metals responsible for fouling such as potassium are generally extracted into the process waters and the volatile matter of the bio-coal is significantly reduced compared to the raw biomass feedstock. It has previously been proposed that HTC reduces the fouling risk due to a combination of decreased oxygen and volatile matter content of the bio-coal [35]. Another potential complication however involves reuptake of metals from the process water onto the surface of the bio-coal. It is known that surface oxygen containing functional groups can bind to cations such as sodium, potassium, magnesium, calcium, which can then be released upon thermal treatment [44]. Binding of alkali metals to the surface of the chars during HTC treatment may result in rapid volatilisation which may still lead to fouling issues. The contribution of this affect requires further investigation but a reduction in O/C would limit readsorption of metals and reduce this potential mechanism. Moreover release of volatile metals, such as potassium, is complicated and the release also depends upon the content of chlorine and silica in the fuels rather than on the potassium content alone [40]. Consequently caution is required when predicting fuel fouling propensity as the hydrothermal process could lead to a greater fouling propensity than would otherwise be expected, due to an increase in the proportion of cations associated with surface functional groups.

4. Conclusions

Discounting moisture, the results have indicated that the inorganic chemistry of the raw *Miscanthus* tested brought about probable slagging and fouling behaviour, whether harvested early or late. This combined with a low HGI would make size reduction to 70% 75 μm, as required in pulverised coal applications challenging without significant energy input. Accordingly, whether *Miscanthus* is harvested early or conventionally, a biomass pre-treatment which improves the fuels ash chemistry and ideally grindability, appears to be a pre-requisite.

Hydrothermal carbonisation at 200 °C showed only limited energy densification for both early and conventionally harvested *Miscanthus*. The HGI increases to 25, resulting in energy savings associated with grinding. HTC at 200 °C reduces fuel alkali metal content although additional reductions in fuel silicon and calcium result in only modest improvement in the ash deformation temperature, suggesting limited improvement in slagging propensity. Nonetheless, the reduction in alkali metals should to a certain extent reduce the potential for deposit formation and combined with a reduction in chlorine and low sulphur content of the fuel, fouling, active oxidation and corrosion should be reduced. Slagging and fouling indices suggested safe combustion for both early and conventionally treated fuels.

HTC at 250 °C results in a significant increase in carbon density and removal of oxygen functionality, with the resulting bio-coal reaching a HHV ranging from 27 to 28 MJ/kg for early and 25 to 26 MJ/kg for conventionally harvested *Miscanthus*. The 'coal like' single stage combustion profile, coupled with a HGI of 150, suggests the fuel will be easy to pulverise, overcoming issues associated with flame stability enabling a good burn interaction if co-fired with coal. HTC at 250 °C can overcome slagging issues and increase the ash deformation temperature from 1040 °C to 1320 °C for early harvested *Miscanthus*. The chemistry also suggests a reduction in fouling and corrosion propensity for both 250 °C treated fuels.

The results indicate that HTC at 250 °C can valorise both conventional and early harvested *Miscanthus*, and that harvesting and processing the crop early does not appear to have any adverse effect on the process yields and combustion properties of the resulting fuel. While the longer term agronomic impacts of early harvesting needs to be fully understood and optimum harvesting time determined, the combustion implications of early harvesting appear to be overcome by HTC and could provide a coal like bio-fuel with increased yields up to 40% per hectare due to avoidance of overwinter dry matter loss.

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