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Full Length Article

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 over-wintering 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