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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.

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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 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.

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_nK_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:

$$\mathrm{HHV} = 3.55C^2 - 232C - 2230H + 51.2C \times H + 131N + 20,600 \tag{E.1}$$

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 $\mathrm{SAN}^{\mathrm{PLUS}}$ 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