Miscanthus as a feedstock for fast-pyrolysis: Does agronomic treatment affect quality?

E.M. Hodgson [a], R. Fahmi [c], N. Yates [b], T. Barraclough [b], I. Shield [b], G. Allison [a], A.V. Bridgwater [c], I.S. Donnison [a,*]

[a] Institute of Biological, Environmental, and Rural Sciences, Aberystwyth University, Gogerddan, Aberystwyth, Ceredigion SY23 3EB, UK
[b] Rothamsted Research, Harpenden, Hertfordshire AL5 2JQ, UK
[c] Bioenergy Research Group, School of Chemical Engineering and Applied Chemistry, Aston University, Birmingham B4 7ET, UK

ARTICLE INFO

ABSTRACT

The objectives of the experiment were to assess the impact of nitrogen (N) and potassium (K) fertiliser application on the cell wall composition and fast-pyrolysis conversion quality of the commercially culti-vated hybrid Miscanthus x giganteus. Five different fertiliser treatments were applied to mature Miscan-thus plants which were sampled at five intervals over a growing season. The different fertiliser treatments produced significant variation in concentrations of cell wall components and ash within the biomass and affected the composition and quality of the resulting fast-pyrolysis liquids. The results indicated that application of high rates of N fertiliser had a negative effect on feedstock quality for this conversion pathway: reducing the proportion of cell wall components and increasing accumulation of ash in the harvested biomass. No exclusive effect of potassium fertiliser was observed. The low-N fertil-iser treatment produced high quality, low ash–high lignin biomass most suitable as a feedstock for thermo-chemical conversion.

© 2010 Published by Elsevier Ltd.

1. Introduction

Due to the rise in demand for renewable energy, dedicated bio-mass energy crops such as the Asian C4 grass Miscanthus are becoming more widely cultivated across Europe, predominantly for use as a feedstock for thermo-chemical conversion. Miscanthus x giganteus is the most widely cultivated Miscanthus genotype for commercial production of lignocellulosic biomass. The biomass produced is predominantly used as a feedstock for generation of heat and power via combustion processes such as co-firing with coal. However, Miscanthus also represents a key candidate crop for use in biomass to liquid conversion processes and biorefineries to produce a range of liquid fuels and chemicals by processes such as fast-pyrolysis.

1.1. Fast-pyrolysis conversion to fuels and products

Fast-pyrolysis is a technology currently receiving considerable interest as a means of producing liquid fuels and a range of special-ity and commodity chemicals. The main advantage of fast-pyrolysis is the production of a liquid product which can be easily and eco-nomically transported and stored (Brammer et al., 2006) thereby de-coupling the handling of solid biomass from utilisation. Pyroly-sis liquid, commonly referred to as 'bio-oil', constitutes a micro-emulsion of the intermediate degradation products of the plant cell wall polymers cellulose, hemicellulose, and lignin (Bridgwater, 2007). The elemental composition of the pyrolysis liquids approxi-mates to that of the biomass feedstock used (Diebold, 1999; Oasmaa and Czernik, 1999). Pyrolysis liquid represents a low cost liquid biofuel with a positive carbon balance (Chiaramonti et al., 2007) capable of providing a substitute for mineral fuel oils with potential to be used in small to large scale (co-firing) power gener-ation systems (Brammer et al., 2006; Bridgwater et al., 2002; Chiaramonti et al., 2007; Oasmaa and Czernik, 1999). In terms of its use in a bio-refinery system, a wide range of products may be re-fined from biomass derived pyrolysis liquids including sugars, agri-chemicals, food flavourings, adhesives, fuel additives, and emission reduction agents (Radlein, 1999). However, the range, quantity, and quality of achievable products depends greatly on the type and composition of the biomass feedstock used (Boateng et al., 2006; Diebold, 1999; Fahmi et al., 2007). Pyrolysis liquid yields, based on the dry weight of biomass fed, typically range from around 70–75% for wood (Bridgwater, 2003) and 55–65% for grasses (Bridgwater, 2007).

1.2. Biomass feedstock quality criteria for thermo-chemical conversion

In terms of combustion, heating value represents an important quality parameter. Variation in heating value of biomass feedstocks predominantly derive from variation in cell wall composition and concentrations of moisture and ash (Lewandowski et al., 2003). High moisture content in biomass causes a reduction of its heating value and an overall decrease of combustion efficiency. This is a result of inhibition of ignition and an increased volume of flue gas produced during combustion (Lewandowski and Kicherer, 1997; McKendry, 2002). This in turn reduces the overall combustion temperature leading to incomplete combustion of the feedstock and an increase in the evolution of harmful gases such as CO, NO_x and SO_2 (Lewandowski and Kicherer, 1997). Biomass ash has a relatively low melting point, the occurrence of ash melting during thermal processing results in the production of 'slag' which, when deposited inside combustion chambers or boilers, results in a reduction of heat transfer and an overall reduction in the efficiency of combustion (Lewandowski and Kicherer, 1997). In addition, high concentrations of alkali metals can lead to accumulation of corrosive chemicals (KCl and HCl) within the combustion equipment (Lewandowski and Kicherer, 1997; McKendry, 2002). The oxygen concentration of a material also has a strong effect on its heating value when combusted. For example, heating value has been shown to decrease almost linearly as oxygen concentration increases (Lewandowski and Kicherer, 1997). It has been suggested that the proportion of lignin contained within the material can be used as an indicator of its heating value (Demirbas, 1997; Friedl et al., 2005). Lignin has a lower oxygen concentration (<300 g kg^{-1}) than holocellulose (>500 g kg^{-1}), and as a result the heating value of lignin (24,000 kJ kg^{-1}) is much higher than that of holocellulose (15,000 kJ kg^{-1}) (Lewandowski and Kicherer, 1997). Therefore, the greater the ratio of lignin to holocellulose the higher the heating value of the biomass.

For conversion via fast-pyrolysis, feedstock quality criteria depend on whether the pyrolysis liquid product is to be used directly as a fuel or as an intermediate product in a bio-refinery. In both cases cell wall composition of the feedstock greatly influences the characteristics of the pyrolysis liquid and the range of products which can be subsequently refined (Fahmi et al., 2008; Oasmaa et al., 2002; Yang et al., 2007; Zabaniotou et al., 2008). The lignin concentration of the feedstock has both beneficial and detrimental effects in terms of pyrolysis liquid quality. For example, high lignin concentrations confer higher heating value to the product liquid (Demirbas, 1997; Friedl et al., 2005) and increased yields of phenolic compounds (Amen-Chen et al., 2001; Effendi et al., 2008), however high lignin feedstocks have also been observed to produce more viscous and unstable pyrolysis liquids (Fahmi et al., 2008; Pattiya et al., 2008). The presence of high ash concentrations has also been shown to have a detrimental effect on the product yield and quality of pyrolysis liquids. Ash is known to have a catalytic effect on thermal decomposition, higher ash concentrations giving rise to higher yields of char and gas at the expense of the liquid product yield (Fahmi et al., 2007). The presence of high ash concentrations in the feedstock has also been shown to confer poor thermal stability to the liquid product (Fahmi et al., 2007, 2008; Pattiya et al., 2008) and a reduction of its heating value. This results from increased yields of reaction water formed by catalytic cracking of vapours due to the increased production of char (Diebold, 1999; Fahmi et al., 2007, 2008). The thermal stability greatly affects the duration for which pyrolysis liquids can be stored. As only partial decomposition of the biomass occurs during fast-pyrolysis, polymerisation and condensation reactions continue to occur in the liquid during storage (Oasmaa and Kuoppala, 2003). The effects of this 'aging' include an increase in viscosity, density, and water content, and a decrease in molecular homogeneity and heating value (Fahmi et al., 2008; Oasmaa and Kuoppala, 2003).

1.3. Miscanthus as a feedstock for combustion and fast-pyrolysis

In comparison with other lignocellulosic biomass crops, *Miscanthus* has been shown to contain significantly lower concentrations of moisture and ash (Lewandowski and Kicherer, 1997) which are favourable feedstock characteristics for both combustion and pyrolysis processes. Delay of the crop harvest by 3–4 months (to February/March) has been shown to further reduce concentrations of moisture and ash, but does so at the expense of dry matter yield (Lewandowski et al., 2003). The influence of agronomic practice (e.g. inorganic fertiliser application) is also likely to influence the dry matter yields and the levels of inorganics present in the harvested biomass. Several studies have been performed to determine the effects of inorganic fertiliser inputs on the productivity of this commercial genotype (Cosentino et al., 2007; Danalatos et al., 2007; Ercoli et al., 1999; Schwarz et al., 1994), however a lack of knowledge exists regarding the impacts of N and K fertiliser inputs on *Miscanthus* composition and quality in terms of its use as a feedstock for thermal conversion technologies.

2. Methods

2.1. Fertiliser application field trials

Field trials were carried out by Rothamsted Research (Harpenden, UK) as part of the Supergen Bioenergy Research project. The field trial was conducted at Woburn Experimental Farm (Bedfordshire, UK). The field trial occupied a total area of 0.69 ha^{-1} subdivided into 42 plots each with an area of 0.012 ha^{-1}. Fourteen fertiliser treatments (Table 1) were applied using a randomised block design with three replicate blocks. *Miscanthus x giganteus* clones were obtained from ADAS holdings Ltd. (Wolverhampton, UK) and planted using rhizome pieces at a spacing of 3.5 plants m^{-2}. The soil type was a Cottenham and Stackyard series sandy loam (Catt et al., 1980). Nitrogen fertiliser was applied in the form of ammonium nitrate, and potassium fertiliser was applied in two forms, potassium chloride and potassium sulphate.

The site was planted in April 2003 and plant material sampled at five time points over the 2005–2006 growing season (Table 2). At each sampling, tillers were counted in 2 m of a row (1.5 m^2 area). In the first three samplings material was separated into leaf and stem, however, this was not possible after the third sampling as little or no leaf material (<0.5 g) was present as a result senescent leaf

Table 1
Fertiliser treatments applied and subset selected for cell wall analysis and fast-pyrolysis trials.

Treatment	N	KCl	K_2SO_4	Blocks	Plot No.
1[a]	0	50	0	3	02, 15, 33
2	50	100	0	3	01, 19, 41
3	50	0	0	3	03, 22, 38
4	50	0	50	3	04, 26, 36
5	50	50	0	3	05, 24, 29
6	50	0	100	3	07, 21, 39
7	100	50	0	3	13, 27, 42
8	150	100	0	3	06, 18, 31
9	150	0	100	3	09, 16, 32
10[a]	150	0	0	3	10, 17, 37
11[a]	150	50	0	3	11, 23, 35
12[a]	150	0	50	3	12, 20, 34
13	200	50	0	3	14, 28, 40
14[a]	250	50	0	3	08, 25, 30

[a] Selected treatments.