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Characterisation of spruce, salix, miscanthus and wheat straw for pyrolysis applications

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HIGHLIGHTS

- ▶ Compositional analysis and pyrolytic characterisation of lignocellulosic biomasses.
- ▶ Herbaceous biomass contains more ash and xylose compared to woody biomass.
- ▶ Decreased temperature of maximum decomposition for high ash feedstocks (TGA).
- ▶ Lignin-derived compounds indicative of lignin structure in biomass (Py-GC/MS).
- ▶ Decomposition of hollocellulose components influenced by alkali metals in ash.

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ABSTRACT

This research details the characterisation of four Irish-grown lignocellulosic biomasses for pyrolysis by biomass composition analysis, TGA, and Py-GC/MS-FID. Ash content (mf) increased in the order spruce (0.26 wt.%) < salix (1.16 wt.%) < miscanthus (3.43 wt.%) < wheat straw (3.76 wt.%). Analysis of hydrolysis-derived sugar monomers showed that xylose concentrations (4.69–26.76 wt.%) ranged significantly compared to glucose concentrations (40.98–49.82 wt.%). Higher hemicellulose and ash contents probably increased non-volatile matter, and decreased the temperature of maximum degradation by TGA as well as yields of GC-detectable compounds by Py-GC/MS-FID. Differences in composition and degradation were reflected in the pyrolysate composition by lower quantities of sugars (principally levoglucosan), pyrans, and furans for salix, miscanthus, and wheat straw compared to spruce, and increased concentrations of cyclopentenones and acids.

1. Introduction

EC Directive (2009/28/EC) requires a substitution of 16% of gross final energy consumption with renewable energy by 2020, with biomass expected to play an important role. In Ireland, biomass resource assessments have shown that a portion of demand can be met by waste and residue contributions. For example, sawmill residues (predominantly spruce) totalled 845,000 m^3 in 2010. Furthermore, between 80 and 325 kt of agricultural straw residues could also be available for bioenergy applications. Wheat straw in particular does not have significant markets, apart from the animal husbandry sector and mushroom composting sector. It is expected that remaining biofuel requirements can be met by processing energy crops (Hayes et al., 2009). In recent years, government grants have aided the establishment of miscanthus and salix in Ireland, with current acreage lying at approximately 2600 ha and 1100 ha, respectively (Jossart, 2011). On suitable land, miscanthus is generally favoured over salix due to greater yields and lower disease risks (Hayes et al., 2009).

The substitution of transport fuels is perhaps the most challenging aspect of the renewable energy target. While research into biomass conversion technologies is on-going, no single dominant technology has emerged for large-scale development (Sims et al., 2009). In recent times, there has been significant interest in integrated biorefinery concepts, whereby several biomass feedstocks and conversion technologies may be employed in parallel or in series for the production of biofuels or biochemicals (Melero et al., 2012).

Fast pyrolysis is a thermochemical conversion process occurring in inert atmospheres at moderate temperatures (500 °C). The most important parameters for fast pyrolysis include high heating rates and good heat transfer, pyrolysis temperature, and low vapour

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residence times. In standard configuration, fast pyrolysis of a clean wood biomass yields a liquid organic "bio-oil" (75%), charcoal (12%), and gas (13%). For transport fuel applications, further upgrading of bio-oil is required (Bridgwater, 2007). An attractive advantage of pyrolysis and upgrading is that it is more cost-effective when compared with technologies like biomass gasification with methanol or Fischer–Tropsch synthesis (Haq, 2012). Recent developments in the pyrolysis sector have been described by Butler et al. (2011) and Venderbosch and Prins (2010). A concept which has gained significant attention is delocalised pyrolysis followed by upgrading to transport fuels in a central facility. This might include gasification of bio-oil followed by synthesis of liquid fuels (Dahmen, 2010), or integration of bio-oil upgrading with adapted refinery infrastructure. To achieve the latter goal, it is widely accepted that bio-oil would first need to be processed in a two stage hydrotreatment and hydrodeoxygenation process before co-processing with petroleum derivatives in a fluidised catalytic cracking unit (Elliott, 2007).

Considering the scales of operation required for competitive transport fuel production, a feedstock flexible pyrolysis facility is advantageous. However, the composition of lignocellulosic biomass and thus the quality of the bio-oil product can vary, which is important when considering downstream processing or upgrading operations.

Several authors have previously compared different biomass feedstocks for analytical pyrolysis (Azeez et al., 2010; Greenhalf et al., 2012; Ralph and Hatfield, 1991; Torri et al., 2010) and applied pyrolysis approaches (Fahmi et al., 2008; Oasmaa et al., 2009; Piskorz et al., 1988). The objective of this study is to compare the pyrolytic decomposition and products of four different types of Irish-grown biomass by Py-GC/MS-FID and TGA, and to provide a better understanding of the possible industrial implications of fast pyrolysis as a conversion technology for biofuels and biochemicals. It should however be noted that GC-detectables account for approximately 40 wt.% of the condensable pyrolysate.

2. Methods

2.1. Biomass feedstocks

Spruce shavings, short rotation coppice willow (salix), miscanthus, and wheat straw were investigated in this study. The latter two feedstocks were procured from the University College Dublin Research Farm at Lyons Estate, Newcastle, Kildare, Ireland. The salix was sourced from Rural Generation Limited, Derry, Northern Ireland, while the spruce shavings (without bark) were acquired from an Irish Sawmill.

2.2. Characterization of biomass

Ash content was determined gravimetrically-oven-dry biomass samples were pre-ashed and heated in a Heraeus furnace at 520 °C for 6 h. Volatile content and thermogravimetric curves were obtained from a thermogravimetric analyser (Netzsch STA 449F3). Vacuum-dried biomass samples (10 mg) were heated from room temperature to 700 °C at 10 °C/min in a nitrogen atmosphere and held for 5 min. The fixed carbon content of the biomass samples was calculated by subtraction. The complete oxidation method was used for elemental analysis of biomass samples on a CE Instruments CHNS Flash 1112 Analyzer system.

For extractives determination, biomass samples were successively extracted with petroleum benzene, acetone and 70% methanol in water, with each extraction lasting 12 h. Extracted samples were subsequently used for determination of holocellulose and lignin content. Sample preparation consisted of a two-step hydrolysis step. For the prehydrolysis step 2 ml of 72% H_2SO_4 was added to 200 mg of the sample and was hydrolysed for 1 h. The reaction was terminated by addition of 6 ml of distilled water. Post-hydrolysis was carried out at 120 °C under pressure for 50 min using a Systec VX-75 autoclave (Systec GmbH, Germany). The hydrolysed sample was made up to the 100 ml mark with distilled water and allowed to cool, followed by filtration through a 0.45 μm glass-frit filter. Residue was dried at 105 °C and gravimetrically determined for condensed lignin, and an aliquot of the supernatant was taken for sugar analysis on a high-performance borate-complex anion-exchange chromatography Ultimate 3000 (Dionex Corporation) equipped with a 6.6 mm Omnifit bore column of 115 mm length. The column is packed with a strong anion exchange resin (MCI Gel CA08F (Mitsubishi) at 60 °C. The mobile phase was made of (A) 0.3 M potassium borate buffer pH 9.2 and (B) 0.9 M potassium borate buffer pH 9.2. A gradient elution of 0.7 ml min^{-1} was used. Separation commenced with 90% A and 10% B, following sample injection with a 35 min linear gradient to 10% A and 90%. Data acquisition lasted 47 min. Sugars were quantified after column derivatisation with Cu-bichinconiate according to previous authors (Willför et al., 2009).

For ICP analysis, vacuum-dried biomass samples were hydrolysed prior to measurement. Hydrolysis involved digesting 100 mg of finely milled sample with 2 ml 70% nitric acid on a START 1500 Digestion Microwave (MLS GmbH, Germany) for 10 min at 170 °C and 3 bar. The oven is fitted with pressure control, an automatic turntable, and closed PFA-line digestion vessels with incorporated pressure relief valves. Diluted samples were subsequently analysed on a on a Thermo Scientific iCAP 6300 device.

2.3. Py-GC/MS-FID of biomass samples

In this study, 11 major pyrolysis compounds were calibrated on the Py-GC/MS-FID system. Calibration standards dissolved in an acetone/fluoranthene (internal standard) solution were injected manually. For micropyrolysis experiments, biomass samples were milled using a HERZOG Pulveriser HSM 100A grinding mill under liquid nitrogen. Samples were prepared by spiking stainless steel pyrolysis cups (Eco cup, Frontier Laboratories Ltd.) with 1 μl of internal standard solution with a high precision 5 μl plunger-in-needle syringe (SGE Analytical Sciences, Model 5BR-5). The solution comprised fluoranthene dissolved in acetone at a concentration of 202.95 μg ml^{-1}. Approximately 80 μg of powdered biomass sample were then weighed into the cup and directly pyrolysed on the system. A minimum of three replicates per feedstock were carried out.

The Py-GC/MS-FID system comprised a double shot Py-202iD 2020 microfurnace pyrolyser (Frontier Laboratories Ltd.) mounted on an Agilent 6890 GC system. The system is fitted with a VF-1701 ms (Agilent) fused-silica capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness) and an Aligent 5973 mass selective detector (EI at 70 eV, ion source temperature of 280 °C). Pyrolysis was carried out at 470 °C. The GC oven temperature program started at 45 °C (4 min hold) and was ramped to 280 °C at 3 °C min^{-1} (20 min hold) using He carrier gas at a flow rate of 1 mL min^{-1}. The compounds were identified by comparing their mass spectra profiles to those in NIST and in-house developed libraries.

The quantification calculation employed relative response factors (RRF) obtained via calibration to correlate the relative response of components to mass: $m_x = (A_x.m_{is}/A_{is})\ x\ RRF$ where mx = mass of component x, A_x = FID peak area of component x, m_{is} = mass of internal standard (fluoranthene), A_{is} = FID peak area of internal standard, RRF = relative response factor. RRFs for uncalibrated compounds were estimated based on comparison with an identical GC/MS system.