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Fluidised bed pyrolysis of lignocellulosic biomasses and comparison of bio-oil and micropyrolyser pyrolysate by GC/M-FID.

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Abstract

The fast pyrolysis of Spruce (*Picea abies*), short rotation willow coppice (*Salix alba*), Miscanthus (*Miscanthus x giganteus*), and wheat straw (*Triticum aestivum*) was compared on a laboratory scale bubbling fluidized bed reactor at 460-475 °C. The presence of ash, ranging from 0.26 wt. % for spruce to 3.76 wt. % for wheat straw (moisture free basis) favoured decomposition of cell-wall constituents to char (spruce [11.4 wt. %]< Salix [16.2 wt. %]< Miscanthus [21.8 wt. %] < wheat straw [21.5 wt%]) with a reduction of liquid organic product (spruce [48.3 wt. %]> Salix [41.4 wt. %]>Miscanthus [32.6 wt. %]>wheat straw [30.8 wt. %]). Bio-oils from Miscanthus and wheat straw were inhomogeneous. Differences between absolute masses of compounds determined by GC/MS of the bio-oils compared with Py-GC/MS suggested a greater role of secondary reactions at the fluidised bed scale, reducing concentrations of certain lignin-derived, furan and pyran compounds.

Keywords: fluidised bed, pyrolysis, biomass, biofuel, secondary reactions, ash,

1 Introduction

At present there is significant interest in the development of biomass, biorefinery concepts and associated conversion technologies for the production of biofuels and biochemicals. Although not as developed as other thermal conversion processes like gasification [1], fast pyrolysis of biomass and associated upgrading is deemed to have potential for future development [2]. Concepts for large scale deployment include decentralised pyrolysis of biomass followed by a) centralised gasification of bio-oils and synthesis of biofuels or b) centralised upgrading of bio-oils by a combination of hyrdrotreatment, hydrodeoxygenation, and co-processing with petroleum derivatives in a Fluid Catalytic Cracker. 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 [3]. There is a lag however between the development of fast pyrolysis and associated upgrading technology – while fast pyrolysis technology is available on near commercial scale basis, upgrading technology like bio-oil hydroprocessing technology is currently being scaled from the laboratory to demonstration scales [4, 5].

In Ireland, increased biomass demand for fulfilment of bioenergy substitution commitments is expected to be satisfied from biomass residues like sawmill wastes and agricultural residues, with the balance being made up by dedicated energy crops like Miscanthus or Salix [6]. While pyrolysis is quite a feedstock flexible technology, the cell-wall composition and ash content, which can vary substantially among biomass feedstocks, have a significant bearing on the degradation behaviour of the biomass as well as the physical and chemical quality of the bio-oil product [7-12]. High alkali catalytic activity increases yields of char, and may induce phase separation of bio-oil due to decreased yields of liquid organic product and increased production of water [13]. This problem is particularly pronounced in agricultural residues like straw, where fertiliser requirements and time of harvesting are optimised for food production rather than energy application quality [14].

To screen feedstocks for fast pyrolysis and optimise pyrolysis conditions, there is a need for a rapid and reliable analytical methodology for the provision of primary chemical information on the pyrolysate composition [11]. Py-GC/MS is widely accepted and applied as a model of fast pyrolysis to gather preliminary information on the process. [11, 12, 14, 15] However, the composition of the product bio-oil can vary between the micropyrolyser systems and larger-scale fluidised bed systems, due to various secondary reactions [16, 17].

The objectives of this study are to compare the fluidised bed pyrolysis of four lignocellulosic biomasses with potential for biofuel production applications in Ireland, and to investigate differences in the composition of the (bio-oil) pyrolysate in comparison with a micropyrolysis (Py-GC/MS) system.

2 Materials and Methods

2.1 Preparation and characterisation of lignocellulosic feedstocks

Spruce, Salix, Miscanthus, and wheat straw were employed for this study. The latter two feedstocks were procured from the UCD Research Farm at Lyons Estate, Newcastle, Kildare, Ireland. Chipped Salix was sourced from Rural Generation, Derry, Northern Ireland, while the spruce shavings (without bark) were obtained from an Irish Sawmill. For fast pyrolysis on a fluidised bed reactor, feedstocks were milled on a Retsch cutting mill (model SM 2000) and fractionated (750, 500, 300 μm) on a Retsch sieve shaker over a period of 10 mins. The 300-500 μm fractions obtained were stored in sealed polythene bags. For analytical pyrolysis, samples taken from the 300-500 μm fraction were ground further in a cryogenic mill (HERZOG Pulveriser HSM 100A) and vacuum dried overnight (40 °C and 200 mbar) prior to analytical pyrolysis.

Moisture contents of the feedstocks were determined gravimetrically prior to fast pyrolysis in the fluidised bed unit by drying at 105 °C for 12 hours. A pre-ashing step was carried out before ashing in a Heraeus furnace at 520 ˚C for 6 h, followed by cooling in a desiccator and weighing. For determination volatile matter, 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 minutes. The fixed carbon content of the biomass samples was calculated by subtraction. The procedure used for determination of extractives, Klasson lignin, and biomass sugars by HPAEC-borate is described in literature [15].

2.2 Py-GC/MS-FID experiments

The Py-GC/MS system is a double shot Py-202iD 2020 microfurnace pyrolyser (Frontier Laboratories Ltd.) mounted on an Aligent 6890 GC system. The system is fitted with a DB-1701 (Aligent J&W) fused-silica capillary column (60m x 0.25 mm i.d., 0.25 μm film thickness) and an Aligent 5973 mass selective detector (EI at 70eV, ion source temperature of 280 °C).

Major pyrolysis products were calibrated by one-point calibration on the Py-GC/MS system. Calibration standards dissolved with fluoranthene (internal standard) in acetone were injected manually (1µl). Relative Response Factors (RRFs) were calculated for calibrated compounds and estimated for non-calibrated compounds based on typical responses from the bio-oil GC/MS-FID system. For Py-GC/MS, steel cups (Eco-cup, Frontier Laboratories) were spiked with 1µl of internal standard solution with a high precision 5µl 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 powered biomass sample was then weighed into the cup and analysed on the system. A minimum of three replicates per feedstock were carried out. Pyrolysis was carried out at 470 °C. The GC oven temperature program started at 45 °C (4 min hold) and was ramped to 255 °C at 3 °Cmin^{-1} (70 min hold) using He carrier gas at a flowrate of 1 mL min^{-1}. The compounds were identified by comparing their mass spectra profiles to those in NIST and in-house developed libraries.

2.3 Fluidised bed experiments

Pyrolysis was conducted on a laboratory bubbling fluidized bed unit at a temperature of 475˚C. About 250 g of biomass were used per experiment, which lasted approximately one hour. The system employed has previously been described in literature [15], and comprised a feeding unit (stirred feed container, vibrating tube, and screw feeder), steel reactor (41 mm i.d. x 305 mm), cyclone and charpot, ethanol-cooled condenser (2 ˚C), electrostatic precipitator (-7 kV), and intensive cooler (-20 ˚C). Reactor temperature was controlled manually and temperature was measured with a thermocouple placed in the centre of the fluidised bed (quartz sand, grain size 300-500 µm).

For comparison, pyrolysis was carried out at similar conditions for all feedstocks, namely a pyrolysis temperature of 465-470 ˚C and a pressure drop of 80 mbar. After pyrolysis in the fluidised bed, char was separated from the vapour stream by a cyclone. Most vapours were condensed in the ethanol cooler and the electrostatic precipitator, and drained into a single flask to give bio-oil. Small quantities of aqueous light condensates were collected from the intensive cooler, while non-condensable gasses were vented. System components were weighed before and after each experiment to enable calculation of product yields. Furthermore, internal condenser surfaces were washed with ethanol after pyrolysis, and washings were filtered to enable char and bio-oil residues to be distinguished.

2.4 Bio-oil characterisation and analysis

The Karl Fischer method (according to ASTM D 1744) was employed for determination of water content in bio-oil and condensate fractions on a Schott Titro Line alpha apparatus. Hydranal Composite (34806) was automatically titrated against Hydranal methanol rapid (37817), both supplied by Riedel den Haën.

For determination of pyrolytic lignin, 50 ml of deionised water was vigorously agitated using a kitchen mixer (Gastroback GmbH). Approximately 1 g of bio-oil was added dropwise and the resulting suspension was filtered and vacuum dried at 40 °C and 200 mbar. Any lignin residues remaining on the apparatus were dissolved in ethanol and concentrated by rotary evaporation. Pyrolytic lignin was determined as the sum of the lignin residue on the filter and in the round bottom flask. Bio-oil samples were examined at times 50 magnification with a Keyence digital microscope system (VHX-500F).

The GC/MS-FID system used for bio-oil analysis, was an Agilent 6890 GC system fitted with a DB-1701 (Aligent J&W) fused-silica capillary column (60 m x 0.25 mm i.d., 0.25 µm film thickness) was employed. The system was equipped with FID and an Aligent 5973 mass selective detector. The system was comprehensively calibrated with calibration compounds using fluoranthene as an internal standard, and involved single-point and triple-point calibrations. For bio-oil analysis, filtered solutions (0.45 µm) were prepared with 60 mg of organic material per ml of internal standard solution (202.95 µg fluoranthene per ml acetone). The quantitation calculation employed RRFs obtained by calibration to correlate the relative response of components (from FID) to absolute mass.

3 Results and Discussions

3.1 Fluidised bed pyrolysis of biomass

Feedstock characterisation is presented in Table 1 (proximate and elemental analysis) and Table 2 (biomass composition). Miscanthus and wheat straw compromise higher ash contents, 3.43 wt. % and 3.76 wt. % respectively, compared to Salix (1.16 wt. %) and spruce (0.26 wt. %). Klasson lignin content decreases from 27.73 % for spruce to 15.96 % for wheat straw, while xylose ranged between 4.69 % for spruce to 26.73 % for wheat straw.

During the fluidised bed pyrolysis, feeding of Miscanthus and wheat straw proved more problematic due to a greater production of char. Char aggregates were observed in the bed after pyrolysis trials with these feedstocks. Examination of the bio-oil by microscope confirmed that the spruce and Salix bio-oils were homogenous, while those from Miscanthus and wheat straw were inhomogeneous (Fig. 2). This inhomogeneity is probably due to higher moisture in the starting feedstock and a greater degree of ash catalysis during pyrolysis.

The mass balance of the fluidised bed experiments are presented in Table 3. Organic liquid yield decreased in the order spruce (48.4 wt. %)> Salix (41.4 wt. %)> Miscanthus (32.6 wt. %)> wheat straw (30.8 wt. %). This is likely attributable to a combination of factors including increased portions of hemicellulose and ash, resulting in more char and gas production [18]. Pyrolytic lignin in the bio-oil decreased from 17.5 % for spruce to 7 % for wheat straw. The pyrolytic lignin content of Miscanthus bio-oil was 15.7 wt. %. Wheat straw Klasson lignin content was lower (15.96 wt. %) compared to Miscanthus (21.4 wt. %), but yet char yields were similar - 21.8 wt. % (Miscanthus) and 21.5 wt. % (wheat straw). This suggests that a higher portion of lignin may have been distributed to the char fraction for wheat straw, thus explaining lower pyrolytic lignin content of the oil.

Some of the main compounds quantified in the bio-oils are reported in Table 4, while all compounds quantified in the bio-oil, grouped by chemical family, are presented in Fig. 3. The relative quantities of compounds are representative of cell-wall composition of the biomasses, plus the catalytic effect of ash. Lignin-derived compounds like lignin-derived phenols, guaiacols, and syringols mainly retain their substitution pattern, with spruce bio-oil containing a majority of guaiacol lignin-derived compounds (1.81 wt. %), Salix a majority of syringol lignin-derived compounds (1.0 wt. %), and Miscanthus a significant amount of lignin-derived phenols (0.90 wt. %). Decreasing concentrations of sugars like levoglucosan (spruce [2.22 wt. %]> Salix [0.79 wt. %]> Miscanthus [0.41 wt. %]> wheat straw [0.26 wt%]) are due to alkali catalysed decomposition of cellulose and char catalysed dehydration of levoglucosan [19].

3.2 Comparison of Py-GC/MS-FID with fluidised bed pyrolysis and bio-oil GC/MS-FID

Table 5 compares the quotients of absolute masses of compounds determined by Py-GC/MS-FID and those determined by fluidised bed pyrolysis and GC/MS-FID of the bio-oil. Larger quotients indicate greater differences between absolute masses determined by both methods. Quotients for all compounds were greater than 1, suggesting greater quantitation by the Py-GC/MS-FID method. Nonetheless, it can be seen in Table 5 that quotients for certain compounds were much larger compared to others, suggesting a greater sensitivity of these compounds to secondary reactions during fluidised bed pyrolysis. For example, quotients for 2-hydroxy-2-cyclopenten-1-one, 5-(hydroxymethyl)-2-furaldehyde, and (4H)-3-hydroxy-5,6-dihydro-pyran-4-one were 5.18, 5.0, and 5.7 respectively for straw. Quotients for 4-vinyl phenol, 4-vinyl guaiacol, and 4-vinyl syringol were in a similar range for wheat straw (5.11, 5.46. 5.08 respectively), whereas other lignin derivatives like coniferylaldehyde (7.51), sinapylaldehyde (8.65) and homovanillin (9.64) appeared to be more prone to secondary reactions. Also, indene compounds e.g. 2H-6-hydroxy-5,7-dimethoxy-indene (not shown in Table) detected in small quantities of the micropyrolysis pyrolysate (Salix [0.66 wt. %], spruce [0.30wt. %], Miscanthus [0.16 wt. %], wheat straw [0.18 wt%]) were significantly reduced/not present in bio-oils from fluidised bed pyrolysis.

Trends observed are generally consistent with those observed in literature. Patwardhan et al. [16] observed decreased yields of levoglucosan, furan compounds, and hydroxyacetaldehyde from fluidised bed pyrolysis compared to Py-GC/MS, with increases in low molecular weight compounds and gases [16]. This was suggested to be due to increased times, allowing more secondary reactions to take place. For example, levoglucosan can undergo oligomerisation during transport to the condensers or the condensation process in the fluidised bed [16]. Volatile lignin-derived monomers are also immediately subjected to secondary reactions leading to the formation of oligomers and promote the growth of aerosols in the gas phase prior to recovery of the liquid bio-oil product [17].

Furthermore, it appears that alkali metals in char play a role in the secondary reactions [19]. Considering that the ash content increases in the order spruce (0.26 wt. %)< Salix (1.16 wt. %)< Miscanthus (3.43 wt. %)< wheat straw (3.76 wt. %), it can be observed that the quotients for certain compounds also increase in this order (see Table 5). For example, the quotient for 2-hydroxy-2-cyclopenten-1-one increased in the order spruce (1.73)< Salix (3.06)< Miscanthus (4.07)< wheat straw (5.18), suggesting increased secondary reactions which decrease the yield of this compound from the fluidised bed. Since increased amounts of alkali-containing char were observed in the fluidised bed after Miscanthus and straw pyrolysis experiments, increased cracking of vapour pyrolysis products would be expected.

4 Conclusions

The highest liquid organic yields were achieved in the order spruce (48.3 wt. %)> Salix (41.4 wt. %)> Miscanthus (32.6 wt. %)> wheat straw (30.8 wt. %). A greater degree of cracking reactions in higher ash feedstocks increased yields of char (spruce [11.4 wt. %]< Salix [16.2 wt. %]< Miscanthus [21.8 wt. %] <wheat straw [21.5 wt. %]) and gases. This was also evidenced by decreased yields of levoglucosan from the feedstocks: spruce (2.22 wt. %)> Salix (0.79 wt. %)> Miscanthus (0.41 wt. %)> wheat straw (0.26 wt. %). A greater degree of cracking in pyrolysis of wheat straw compared to Miscanthus may have been responsible for similar yields of char, despite having about 5% less Klasson lignin, and also diminishing pyrolytic lignin in the biooil.

Comparison of absolute masses of compounds in the bio-oil with those from micropyrolysis suggested that certain compounds were more prone to secondary reactions (e.g. oligomerisation or cracking) than others. These compounds include a) lignin-derived monomers with vinyl groups (4-vinyl phenol, 4-vinyl guaiacol, 4-vinyl syringol), b) pyranones e.g. (4H)- 3-hydroxy-5,6-dihydro-pyran-4-one c) certain furanones e.g. 2-5-(hydroxymethyl)-furaldehyde, and d) indenes e.g. 1H-6-hydroxy-7-methoxy-indene were significantly diminished in the pyrolysate prepared by the fluidised bed. Some compounds e.g. coniferylaldehyde, syringaldehyde, homovanillin, 2-hydroxy-2- cyclopenten-1-one appeared to be particularly sensitive to the presence of alkali metals in the fluidised bed. Ultimately the observed differences do not make a significant difference to the overall composition of the bio-oil, but future research could look at comparisons with larger scale reactors.

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