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

12 The fast pyrolysis of Spruce (*Picea abies*), short rotation willow coppice (*Salix alba*), 13 Miscanthus (Miscanthus x giganteus), and wheat straw (Triticum aestivum) was 14 compared on a laboratory scale bubbling fluidized bed reactor at 460-475 °C. The 15 presence of ash, ranging from 0.26 wt. % for spruce to 3.76 wt. % for wheat straw 16 (moisture free basis) favoured decomposition of cell-wall constituents to char (spruce 17 [11.4 wt. %] < Salix [16.2 wt. %] < Miscanthus [21.8 wt. %] < wheat straw [21.5 wt%]) 18 with a reduction of liquid organic product (spruce [48.3 wt. %]> Salix [41.4 wt. 19 %]>Miscanthus [32.6 wt. %]>wheat straw [30.8 wt. %]). Bio-oils from Miscanthus and 20 wheat straw were inhomogeneous. Differences between absolute masses of compounds 21 determined by GC/MS of the bio-oils compared with Py-GC/MS suggested a greater 22 role of secondary reactions at the fluidised bed scale, reducing concentrations of certain lignin-derived, furan and pyran compounds. 23

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

25 1 Introduction

26 At present there is significant interest in the development of biomass, biorefinery 27 concepts and associated conversion technologies for the production of biofuels and 28 biochemicals. Although not as developed as other thermal conversion processes like 29 gasification [1], fast pyrolysis of biomass and associated upgrading is deemed to have 30 potential for future development [2]. Concepts for large scale deployment include 31 decentralised pyrolysis of biomass followed by a) centralised gasification of bio-oils 32 and synthesis of biofuels or b) centralised upgrading of bio-oils by a combination of 33 hyrdrotreatment, hydrodeoxygenation, and co-processing with petroleum derivatives in 34 a Fluid Catalytic Cracker. An attractive advantage of pyrolysis and upgrading is that it 35 is more cost-effective when compared with technologies like biomass gasification with 36 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].

41 In Ireland, increased biomass demand for fulfilment of bioenergy substitution 42 commitments is expected to be satisfied from biomass residues like sawmill wastes and 43 agricultural residues, with the balance being made up by dedicated energy crops like 44 Miscanthus or Salix [6]. While pyrolysis is guite a feedstock flexible technology, the 45 cell-wall composition and ash content, which can vary substantially among biomass 46 feedstocks, have a significant bearing on the degradation behaviour of the biomass as 47 well as the physical and chemical quality of the bio-oil product [7-12]. High alkali 48 catalytic activity increases yields of char, and may induce phase separation of bio-oil 49 due to decreased yields of liquid organic product and increased production of water 50 [13]. This problem is particularly pronounced in agricultural residues like straw, where 51 fertiliser requirements and time of harvesting are optimised for food production rather 52 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.

64 2 Materials and Methods

65 2.1 Preparation and characterisation of lignocellulosic feedstocks

66 Spruce, Salix, Miscanthus, and wheat straw were employed for this study. The latter 67 two feedstocks were procured from the UCD Research Farm at Lyons Estate, Newcastle, Kildare, Ireland. Chipped Salix was sourced from Rural Generation, Derry, 68 69 Northern Ireland, while the spruce shavings (without bark) were obtained from an Irish 70 Sawmill. For fast pyrolysis on a fluidised bed reactor, feedstocks were milled on a 71 Retsch cutting mill (model SM 2000) and fractionated (750, 500, 300 µm) on a Retsch 72 sieve shaker over a period of 10 mins. The 300-500 µm fractions obtained were stored 73 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.

76 Moisture contents of the feedstocks were determined gravimetrically prior to fast 77 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 78 79 cooling in a desiccator and weighing. For determination volatile matter, vacuum-dried 80 biomass samples (10 mg) were heated from room temperature to 700°C at 10°C/min in a 81 Nitrogen atmosphere and held for 5 minutes. The fixed carbon content of the biomass 82 samples was calculated by subtraction. The procedure used for determination of 83 extractives, Klasson lignin, and biomass sugars by HPAEC-borate is described in 84 literature [15].

85 2.2 Py-GC/MS-FID experiments

86 The Py-GC/MS system is a double shot Py-202iD 2020 microfurnace pyrolyser 87 (Frontier Laboratories Ltd.) mounted on an Aligent 6890 GC system. The system is 88 fitted with a DB-1701 (Aligent J&W) fused-silica capillary column (60m x 0.25 mm 89 i.d., 0.25 μ m film thickness) and an Aligent 5973 mass selective detector (EI at 70eV, 90 ion source temperature of 280 °C).

91 Major pyrolysis products were calibrated by one-point calibration on the Py-GC/MS 92 system. Calibration standards dissolved with fluoranthene (internal standard) in acetone 93 were injected manually (1ul). Relative Response Factors (RRFs) were calculated for 94 calibrated compounds and estimated for non-calibrated compounds based on typical 95 responses from the bio-oil GC/MS-FID system. For Py-GC/MS, steel cups (Eco-cup, 96 Frontier Laboratories) were spiked with 1µl of internal standard solution with a high 97 precision 5µl plunger-in-needle syringe (SGE Analytical Sciences, Model 5BR-5). The 98 solution comprised fluoranthene dissolved in acetone at a concentration of 202.95 µg 99 m⁻¹. Approximately 80 µg of powered biomass sample was then weighed into the cup 100 and analysed on the system. A minimum of three replicates per feedstock were carried 101 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 102 carrier gas at a flowrate of 1 mL min⁻¹. The compounds were identified by comparing 103 104 their mass spectra profiles to those in NIST and in-house developed libraries.

105 2.3 Fluidised bed experiments

106 Pyrolysis was conducted on a laboratory bubbling fluidized bed unit at a temperature of 107 475°C. About 250 g of biomass were used per experiment, which lasted approximately 108 one hour. The system employed has previously been described in literature [15], and 109 comprised a feeding unit (stirred feed container, vibrating tube, and screw feeder), steel 110 reactor (41 mm i.d. x 305 mm), cyclone and charpot, ethanol-cooled condenser (2 °C), 111 electrostatic precipitator (-7 kV), and intensive cooler (-20 °C). Reactor temperature was 112 controlled manually and temperature was measured with a thermocouple placed in the 113 centre of the fluidised bed (quartz sand, grain size $300-500 \mu m$).

114 For comparison, pyrolysis was carried out at similar conditions for all feedstocks, 115 namely a pyrolysis temperature of 465-470 °C and a pressure drop of 80 mbar. After 116 pyrolysis in the fluidised bed, char was separated from the vapour stream by a cyclone. 117 Most vapours were condensed in the ethanol cooler and the electrostatic precipitator. 118 and drained into a single flask to give bio-oil. Small quantities of aqueous light 119 condensates were collected from the intensive cooler, while non-condensable gasses 120 were vented. System components were weighed before and after each experiment to 121 enable calculation of product yields. Furthermore, internal condenser surfaces were 122 washed with ethanol after pyrolysis, and washings were filtered to enable char and bio-123 oil residues to be distinguished.

124 **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.

129 For determination of pyrolytic lignin, 50 ml of deionised water was vigorously agitated 130 using a kitchen mixer (Gastroback GmbH). Approximately 1 g of bio-oil was added 131 dropwise and the resulting suspension was filtered and vacuum dried at 40 °C and 200 132 mbar. Any lignin residues remaining on the apparatus were dissolved in ethanol and 133 concentrated by rotary evaporation. Pyrolytic lignin was determined as the sum of the 134 lignin residue on the filter and in the round bottom flask. Bio-oil samples were 135 examined at times 50 magnification with a Keyence digital microscope system (VHX-136 500F).

137 The GC/MS-FID system used for bio-oil analysis, was an Agilent 6890 GC system 138 fitted with a DB-1701 (Aligent J&W) fused-silica capillary column (60 m x 0.25 mm 139 i.d., 0.25 µm film thickness) was employed. The system was equipped with FID and an 140 Aligent 5973 mass selective detector. The system was comprehensively calibrated with 141 calibration compounds using fluoranthene as an internal standard, and involved single-142 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 143 144 fluoranthene per ml acetone). The quantitation calculation employed RRFs obtained by 145 calibration to correlate the relative response of components (from FID) to absolute 146 mass.

147 **3** Results and Discussions

148 **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.

162 The mass balance of the fluidised bed experiments are presented in Table 3. Organic liquid vield decreased in the order spruce (48.4 wt. %)> Salix (41.4 wt. %)> Miscanthus 163 164 (32.6 wt. %)> wheat straw (30.8 wt. %). This is likely attributable to a combination of 165 factors including increased portions of hemicellulose and ash, resulting in more char 166 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 167 168 15.7 wt. %. Wheat straw Klasson lignin content was lower (15.96 wt. %) compared to 169 Miscanthus (21.4 wt. %), but yet char yields were similar - 21.8 wt. % (Miscanthus) and 170 21.5 wt. % (wheat straw). This suggests that a higher portion of lignin may have been 171 distributed to the char fraction for wheat straw, thus explaining lower pyrolytic lignin 172 content of the oil.

173 Some of the main compounds quantified in the bio-oils are reported in Table 4, while all 174 compounds quantified in the bio-oil, grouped by chemical family, are presented in Fig. 175 3. The relative quantities of compounds are representative of cell-wall composition of 176 the biomasses, plus the catalytic effect of ash. Lignin-derived compounds like lignin-177 derived phenols, guaiacols, and syringols mainly retain their substitution pattern, with 178 spruce bio-oil containing a majority of guaiacol lignin-derived compounds (1.81 wt. %), 179 Salix a majority of syringol lignin-derived compounds (1.0 wt. %), and Miscanthus a 180 significant amount of lignin-derived phenols (0.90 wt. %). Decreasing concentrations of 181 sugars like levoglucosan (spruce [2.22 wt. %]> Salix [0.79 wt. %]> Miscanthus [0.41 182 wt. %]> wheat straw [0.26 wt%]) are due to alkali catalysed decomposition of cellulose 183 and char catalysed dehydration of levoglucosan [19].

184 3.2 Comparison of Py-GC/MS-FID with fluidised bed pyrolysis and bio 185 oil GC/MS-FID

186 Table 5 compares the quotients of absolute masses of compounds determined by Py-187 GC/MS-FID and those determined by fluidised bed pyrolysis and GC/MS-FID of the 188 bio-oil. Larger quotients indicate greater differences between absolute masses 189 determined by both methods. Quotients for all compounds were greater than 1, 190 suggesting greater quantitation by the Py-GC/MS-FID method. Nonetheless, it can be 191 seen in Table 5 that quotients for certain compounds were much larger compared to 192 others, suggesting a greater sensitivity of these compounds to secondary reactions 193 during fluidised bed pyrolysis. For example, quotients for 2-hydroxy-2-cyclopenten-1-194 one, 5-(hydroxymethyl)-2-furaldehyde, and (4H)-3-hydroxy-5,6-dihydro-pyran-4-one 195 were 5.18, 5.0, and 5.7 respectively for straw. Quotients for 4-vinyl phenol, 4-vinyl 196 guaiacol, and 4-vinyl syringol were in a similar range for wheat straw (5.11, 5.46, 5.08 197 respectively), whereas other lignin derivatives like coniferylaldehyde (7.51), 198 sinapylaldehyde (8.65) and homovanillin (9.64) appeared to be more prone to secondary 199 reactions. Also, indene compounds e.g. 2H-6-hydroxy-5,7-dimethoxy-indene (not 200 shown in Table) detected in small quantities of the micropyrolysis pyrolysate (Salix 201 [0.66 wt. %], spruce [0.30wt. %], Miscanthus [0.16 wt. %], wheat straw [0.18 wt%]) 202 were significantly reduced/not present in bio-oils from fluidised bed pyrolysis.

203 Trends observed are generally consistent with those observed in literature. Patwardhan 204 et al. [16] observed decreased yields of levoglucosan, furan compounds, and 205 hydroxyacetaldehyde from fluidised bed pyrolysis compared to Py-GC/MS, with 206 increases in low molecular weight compounds and gases [16]. This was suggested to be 207 due to increased times, allowing more secondary reactions to take place. For example, 208 levoglucosan can undergo oligomerisation during transport to the condensers or the condensation process in the fluidised bed [16]. Volatile lignin-derived monomers are 209 210 also immediately subjected to secondary reactions leading to the formation of oligomers 211 and promote the growth of aerosols in the gas phase prior to recovery of the liquid bio-212 oil product [17].

213 Furthermore, it appears that alkali metals in char play a role in the secondary reactions 214 [19]. Considering that the ash content increases in the order spruce (0.26 wt. %) < Salix 215 (1.16 wt. %) < Miscanthus (3.43 wt. %) < wheat straw (3.76 wt. %), it can be observed 216 that the quotients for certain compounds also increase in this order (see Table 5). For 217 example, the quotient for 2-hydroxy-2-cyclopenten-1-one increased in the order spruce 218 (1.73) < Salix (3.06) < Miscanthus (4.07) < wheat straw (5.18), suggesting increased 219 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 220 221 after Miscanthus and straw pyrolysis experiments, increased cracking of vapour 222 pyrolysis products would be expected.

223 **4** Conclusions

224 The highest liquid organic yields were achieved in the order spruce (48.3 wt. %)> Salix 225 (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. 226 227 %]< Salix [16.2 wt. %]< Miscanthus [21.8 wt. %] <wheat straw [21.5 wt. %]) and 228 gases. This was also evidenced by decreased yields of levoglucosan from the 229 feedstocks: spruce (2.22 wt. %)> Salix (0.79 wt. %)> Miscanthus (0.41 wt. %)> wheat 230 straw (0.26 wt. %). A greater degree of cracking in pyrolysis of wheat straw compared 231 to Miscanthus may have been responsible for similar yields of char, despite having 232 about 5% less Klasson lignin, and also diminishing pyrolytic lignin in the biooil.

233 Comparison of absolute masses of compounds in the bio-oil with those from 234 micropyrolysis suggested that certain compounds were more prone to secondary 235 reactions (e.g. oligomerisation or cracking) than others. These compounds include a) 236 lignin-derived monomers with vinyl groups (4-vinyl phenol, 4-vinyl guaiacol, 4-vinyl 237 syringol), b) pyranones e.g. (4H)- 3-hydroxy-5,6-dihydro-pyran-4-one c) certain 238 furanones e.g. 2-5-(hydroxymethyl)-furaldehyde, and d) indenes e.g. 1H-6-hydroxy-7-239 methoxy-indene were significantly diminished in the pyrolysate prepared by the 240 fluidised bed. Some compounds e.g. coniferylaldehyde, syringaldehyde, homovanillin, 241 2-hydroxy-2- cyclopenten-1-one appeared to be particularly sensitive to the presence of 242 alkali metals in the fluidised bed. Ultimately the observed differences do not make a 243 significant difference to the overall composition of the bio-oil, but future research could 244 look at comparisons with larger scale reactors.

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