Pressurised pyrolysis of Miscanthus using a fixed bed reactor

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ABSTRACT

Miscanthus x giganteus was pyrolysed, in a fixed bed reactor in a constant flow of dinitrogen gas, at a rate of 13 °C/min from ambient to 550 °C, then held for 25 min at this temperature. The pressures employed ranged from atmospheric to 26 bar. The major compounds identified in the bio-oil were water, phenol, and phenol derivatives. The water contents impact on the usefulness of the bio-oil as a fuel. However, the phenols could provide useful platform chemicals and products.

The properties of the char were determined using elemental analyses, surface area measurements using the Brunauer–Emmett–Teller equation, a calorimetric bomb, Scanning Electron Microscopy, and 13C NMR spectroscopy. The chars were highly carbonised, especially at the higher pressures, and provided thermally stable materials. Pressure impacted greatly on the surface area. Char formed at atmospheric pressure had a surface area of 162 m²/g, whereas that from the highest pressure applied was only 0.137 m²/g.

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1. Introduction

Much interest has focused in recent years on the utilisation of biomass as alternative sources of fuel largely because biomass can be regarded as a carbon neutral source of energy (Muradov and Vezirioglu, 2008). It also contains very low levels of nitrogen and sulphur.

Pyrolysis, in which biomass feedstock is heated to between 350 and 600 °C or higher in the absence of oxygen (typically in an N2 atmosphere) provides a facile procedure for the conversion of bio- mass into pyrolytic-oil (bio-oil), a char (biochar), and gas (syn-gas). This technique can utilise abundant lignocellulosic feedstocks, which include biomass crops (such as Miscanthus and coppiced willows), agricultural residues, biorefinery wastes, etc. Typically pyrolysis is divided into three modes: fast, intermediate, and slow (Bridgwater, 2006). The mode and conditions used can influence the relative proportions of the three products obtained. Slow pyrolysis uses a low heating rate and a long vapour residence time, and it is used to maximise char yields (Kwapinski et al., 2010). Fast pyrolysis, with a very high heating rate and a short vapour residence time, maximises liquid yields. Although pyrolysis of biomass has achieved commercial status, there still are many aspects of the process that require further study.

Some studies have looked investigated the ways that different process conditions influence the products of biomass pyrolysis and also the various methods used to identify the products formed (Briens et al., 2008, Cao et al., 2010, Stolarek and Ledakowicz, 2005; Wongsiriamnuay and Tippayawong, 2010). Heo et al. (2010) considered Miscanthus as a feedstock taking account of varying parameters such as temperature, particle size, feed rate and gas flow rate. They concluded that temperature was the only factor that had a dramatic influence on product yields.

The influence of pressure on the products of the pyrolysis of biomass has been largely overlooked. A study of the pressurised pyrolysis of wheat straw by Mahinpey et al. (2009) has indicated that reactor pressure has a significant influence on both the yields and the quality of the products obtained. However, that work looked at a narrow range of reaction pressures, 0.689 (10 psi) to 2.758 bar (40 psi). It was concluded that 1.379 bar (20 psi) is the optimum pressure with respect to the product yields for the pyrolysis of wheat straw in a tubular reactor. Fjellerup et al. (1996) worked with pulverized wheat straw in a pressurised entrained flow reactor at pressures of 10 and 20 bar and temperatures of 700–1000 °C. They concluded that the final product yield under the two pressures was very similar. The focus on char in the study of Whitty et al. (2008a) suggested that pressurised pyrolysis of kraft liquors resulted in a reduction of the char particle size as the pressure was increased. However, the opposite was observed by Mahinpey et al. (2009) for a wheat straw feedstock.

There are data to indicate large differences in the yields and properties of the products from the pyrolysis of different feedstocks. This statement is based on a study by Özçimen and Ersoy-Meriçboyu (2010). That study looked at several different feedstocks, such as apricot stones, hazelnut shells, chestnut and grape seeds. The results showed that pyrolysis of these materials under the same conditions gave products that were significantly different. The major differences were in the surface areas of the...
chars and the quantities of the various compounds identified in the bio-oil. The yields of bio-oils ranged from about 28% to 40%. That suggests that studies carried out on a particular feedstock can be used only as a rough guideline with regard to what might be expected for different feedstocks.

There have been more extensive studies on the influences of pressure on the pyrolysis of coal. Roberts et al. (2003) found that yields of coal pyrolysis products (liquid and gas) decreased at elevated pressures, but not in any predictable manner. The major differences were in the morphologies of the chars produced, and the morphologies and porosities of the chars have been shown to be greatly influenced by pressure within the reactor (Matsuoka et al., 2005). However, it is unlikely that valid comparisons can be made between products from the pyrolysis of coal and of biomass because the types of bonds in coal and in biomass substrates are very different. The major components of biomass are cellulose and hemicelluloses with glycosidic linkages between the sugar molecules, and lignin with ether linkages between the aromatic components and between the aromatic functionalities and the phenylpropane components. The energy needed to cleave these bonds (380–420 kJ/mol) is far less than that for cleavage of the polycyclic aromatic components. The energy needed to cleave these bonds (380–420 kJ/mol) is far less than that for cleavage of the polycyclic aromatic components. However, it is unlikely that valid comparisons can be made between products from the pyrolysis of coal and of biomass because the types of bonds in coal and in biomass substrates are very different.

The energetic nature for the lower HHV (MJ/kg) values (Table 1).

The theoretical high heating values (HHV) for char and bio-oil were determined by carrying out analyses on selected samples using a Parr 6200 calorimeter. The HHV (MJ/kg) were also calculated using Eq. (1) developed by Friedl et al. (2005), based on the carbon, hydrogen, and nitrogen contents from the elemental analyses.

\[
HHV = 1.87 \cdot C^2 - 144 \cdot C - 2820 \cdot H + 63.8 \cdot C \cdot H + 129 \cdot N + 20147
\]  

(1)

The accuracy of the data obtained using Eq. (1) was checked by comparing with the measurements made. Data were closely comparable for the higher HHV values, but there was lesser comparability for the lower HHV (MJ/kg) values (Table 1).

A Varian Saturn 3400 Gas Chromatography/Mass Spectrometry (GC/MS) instrument with an ion trap detector was used for bio-oil analyses. A Varian VF5-MS column (5% phenyl, 95% dimethylpolysiloxane low bleed phase, 30 × 0.25 mm id × 0.25 μm) was used. The oven was programmed to hold at 45 °C for 3 min, then ramped up at a rate of 3 K/min to 280 °C and held for 15 min. The injector was set at 250 °C, and the injector split ratio was 30:1. The carrier gas was helium, with a constant flow rate of 1 cm³/min. To prepare the samples for the GC/MS the bio-oil was first filtered using a 0.45 μm filter, then made up in acetone to an approximately 6% solution. Floroanthene was used as an internal standard for quantification.

The 13C VACP-MAS NMR solid state (Peersen et al., 1993) spectra were acquired using a Varian Spectrometer at 500 MHz. All the experiments were carried out at room temperature. The rotors were spun, using dry air, at 15 kHz. The conventional single contact 1H-13C pulse sequence in the rotating frame, and high power proton decoupling during signal acquisitions, were applied. Proton τ/2 pulses of 2.85 μs and optimized cycle delays of 0.5 s were used.

3. Results and discussion

3.1. Product yield

Fig. 1 shows the mass percent of the three products obtained from pyrolysis at different pressures. There was little difference between the yields of char obtained for pyrolysis at any of the pressures applied. Whitty et al. (2008b) reported that (similar to our studies with MxG) there was very little difference in char yields from a feedstock of black liquor at temperatures below 800 °C and pressures of 10 and 20 bar (similar to our study with MxG). Work carried out by Mahinpey et al. (2009) on the pressurised pyrolysis of wheat straw also showed very little difference in the yields of char. However, Mahinpey et al. (2009) showed that the yield of oil increased, and that of gas decreased as the reaction pressure increased. These data indicate that product recovery was influenced by the pressure within the reactor. However, the results from the pyrolysis of our MxG feedstock are different. Each experiment was repeated three times, and the total relative yield of bio-oil remained at a rather constant level, and an increase was observed only for the 16 bar pressure. There was also a difference in the yields of the three different fractions of bio-oil obtained, as indicated from Fig. 2. The maximum tar yield was obtained at atmospheric pressure. As the reaction pressure increased the yield of the heavy fraction (tar) decreased. This may be explained by the
fact that the tar became trapped on the char at the higher pressures, leading to secondary decomposition. The maximum yield of the middle fraction was obtained at 11 bar, and the minimum yield of the light fraction was obtained at that pressure. The light fraction was the most abundant at all pressures. However, this fraction was primarily composed of water.

### 3.2. Characterisation of bio-oil

The O/C, H/C ratios, on a moisture free basis, and the HHV for the crude bio-oil are given in Table 1. As the reaction pressure increased the carbon content of the heavy fraction increased, and thus the HHV also increased. This can also be explained by the slow removal of the tar from the reactor and secondary decomposition occurred. During the secondary reactions greater amounts of oxygen and hydrogen, than of carbon, were removed from the tar. The oxygen and hydrogen atoms were possibly removed as water and became part of the light fraction. The light fraction had mostly a negative HHV, whereas the heavy fraction has a much higher HHV (all the HHV were calculated on a crude basis, i.e. with water).

The oxygen and hydrogen contents of the bio-oils and tar produced do not appear to follow any predictable pattern. With the exception of the value for the tar, the carbon content increased as the pressure increased. The lowest O content was achieved from the tar produced at 26 bar: this bio-oil also had the highest theoretical heating value, 30.9 MJ/kg.

![Fig. 1. Mass balances of products obtained at the different pressures. Experimental data are compared with the results of Mahinpey et al. (2009).](image1)

![Fig. 2. Yields of the three bio-oil fractions, as percentages of the total bio-oils recovered.](image2)

![Fig. 3.](image3)

### Table 1
Elemental composition and high heating values (HHV) of the three fractions of bio-oil.

<table>
<thead>
<tr>
<th>Pressure bar</th>
<th>Water content, wt.%</th>
<th>C, wt.%</th>
<th>H, wt.%</th>
<th>N, wt.%</th>
<th>O/C (dry)**</th>
<th>H/C (dry)**</th>
<th>HHV Eq. (1) MJ/kg</th>
<th>HHV (measured) MJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Heavy Fraction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>*</td>
<td>49.19</td>
<td>7.839</td>
<td>0.756</td>
<td>0.923</td>
<td>0.161</td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>*</td>
<td>49.24</td>
<td>5.337</td>
<td>0.747</td>
<td>0.892</td>
<td>0.149</td>
<td>19.5</td>
<td>17.9</td>
</tr>
<tr>
<td>11</td>
<td>*</td>
<td>50.47</td>
<td>5.175</td>
<td>0.692</td>
<td>0.864</td>
<td>0.103</td>
<td>19.9</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>*</td>
<td>62.77</td>
<td>9.583</td>
<td>0.199</td>
<td>0.437</td>
<td>0.153</td>
<td>30.0</td>
<td>29.96</td>
</tr>
<tr>
<td>21</td>
<td>*</td>
<td>69.06</td>
<td>5.003</td>
<td>1.002</td>
<td>0.361</td>
<td>0.072</td>
<td>27.3</td>
<td>27.78</td>
</tr>
<tr>
<td>26</td>
<td>*</td>
<td>67.02</td>
<td>8.082</td>
<td>0.476</td>
<td>0.061</td>
<td>0.067</td>
<td>30.9</td>
<td></td>
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<tr>
<td><strong>Middle fraction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1</td>
<td></td>
<td>42.57</td>
<td>14.61</td>
<td>8.673</td>
<td>0.661</td>
<td>0.509</td>
<td>0.0363</td>
<td>20.3</td>
</tr>
<tr>
<td>6</td>
<td>*</td>
<td>49.24</td>
<td>5.337</td>
<td>0.747</td>
<td>0.892</td>
<td>0.149</td>
<td>19.5</td>
<td>17.9</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>50.71</td>
<td>17.49</td>
<td>8.107</td>
<td>0.208</td>
<td>0.039</td>
<td>0.038</td>
<td>4.56</td>
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<tr>
<td>16</td>
<td>*</td>
<td>51.21</td>
<td>6.029</td>
<td>0.367</td>
<td>3.271</td>
<td>0.149</td>
<td>6.23</td>
<td>5.37</td>
</tr>
<tr>
<td>21</td>
<td>*</td>
<td>66.34</td>
<td>29.81</td>
<td>7.261</td>
<td>0.699</td>
<td>0.259</td>
<td>0.024</td>
<td>11.1</td>
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<tr>
<td>26</td>
<td>*</td>
<td>37.03</td>
<td>18.32</td>
<td>8.169</td>
<td>0.177</td>
<td>1.304</td>
<td>0.129</td>
<td>4.82</td>
</tr>
<tr>
<td><strong>Light fraction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>56.56</td>
<td>6.642</td>
<td>6.523</td>
<td>0.387</td>
<td>2.366</td>
<td>0.016</td>
<td>3.81</td>
</tr>
<tr>
<td>6</td>
<td>*</td>
<td>21.97</td>
<td>8.790</td>
<td>10.81</td>
<td>0.228</td>
<td>5.379</td>
<td>0.745</td>
<td>–5.23</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>79.95</td>
<td>7.022</td>
<td>9.496</td>
<td>0.143</td>
<td>2.685</td>
<td>0.271</td>
<td>–3.11</td>
</tr>
<tr>
<td>16</td>
<td>*</td>
<td>63.55</td>
<td>5.015</td>
<td>9.642</td>
<td>0.149</td>
<td>2.085</td>
<td>0.188</td>
<td>–4.44</td>
</tr>
<tr>
<td>21</td>
<td>*</td>
<td>72.27</td>
<td>5.076</td>
<td>7.473</td>
<td>0.254</td>
<td>0.229</td>
<td>0.177</td>
<td>–11.3</td>
</tr>
<tr>
<td>26</td>
<td>*</td>
<td>59.634</td>
<td>4.822</td>
<td>10.29</td>
<td>0.291</td>
<td>2.634</td>
<td>0.306</td>
<td>–6.14</td>
</tr>
</tbody>
</table>

Note: *Unable to measure.

**The elemental composition was recalculated, minus the oxygen and hydrogen present as water.**
bio-oil will allow much better separation in the GC and thus will allow more accurate identifications of the compounds present.

Pressure had very little influence on the types of compounds identified in the bio-oil. However, the quantities of the various compounds that were identified varied greatly, particularly when compared to other studies of the pyrolysis of biomass (Mullen and Boateng, 2008). Phenol was the most abundant compound present in all of the bio-oil fractions, and that also corresponds with most of the data in the literature. However, phenol was in much greater abundance in the bio-oil produced in this than in most other studies. In some cases the phenolic compounds made up as much as 64 wt.% of the bio-oil (moisture free). Phenol and many of the phenolic compounds are valuable commercially. One of the major differences between the bio-oil produced in this study and the bio-oil described by some researches (Mullen and Boateng, 2008; Zhang et al., 2007) is the remarkably low levels of carboxylic acids and high levels of water in the bio-oil. High water content in the light fraction is due to the low heating rate used during these experiments. Bridgwater et al. (1999) have pointed out that low heating rates lead to increased char formation, and hot char can act as a catalyst causing secondary cracking of organic vapour to form secondary char, water, and gases.

3.3. Characterisation of char

The effects of the reaction pressure on the elemental composition of char are shown in Table 2. As a consequence of the pyrolysis process, the carbon content of the residual material increased and the oxygen content decreased as a result of the loss of functional groups during the process. A decrease in the hydrogen content was also noted. A large fraction of the oxygen and hydrogen was lost as water. As the pressure increased the carbon content also increased. However, the maximum carbon content was achieved at 16 bar. It may be possible that tar is unable to exit the reactor at the elevated pressures and thus becomes trapped on the char.

In contrast to our observations for MxG, Matsuoka et al. (2005) observed that coal swells notably at high pressure giving rise to a more porous char product. Whitty et al. (2008a) also noted swelling of the paper pulp residue arising from pressurised pyrolysis.

Considerable differences were observed for the surface area of the char produced at different pressures. A maximum surface area was obtained for char produced at atmospheric pressure (161.7 m²/g), and the area decreased rapidly as the pressure was increased (for 2, 6, 11, 16, 21 and 26 bar the surface area was 15.85, 2.258, 1.366, 0.778, 0.535 and 0.137 m²/g, respectively). The low surface area of char produced under high pressure is largely due to the trapping of tar on the surface of the char and also the collapse of the pore structures, particularly at the higher pressures. Cetin et al. (2005) also noted that char generated under atmospheric pressure and at a low heating rate exhibited a microporous structure, and thus a large surface area, whereas char generated under increased pressures contained large amounts of macropores. This can largely be attributed to the melting and trapping of volatile material, which causes the micropores to become clogged. SEM images presented in Fig. 4 show the morphologies of the chars prepared under different pressures. A very distinctive honeycomb structure, responsible for the high char surface area, is evident in the char produced under the lower pressures. As the pressure of pyrolysis increased the structure collapsed, resulting in much lower surface areas. This was confirmed by the BET results. The NMR spectra (Fig. 5) show the symmetrical aromatic resonances characteristic of chars. There is up field resonance shift from about 132 to 128 ppm evident for the spectra at 16 and 26 bar. Mention was made of the increase in the carbon content of the char as the pressure was raised. That and the resonance shift can be explained by a progression of the aromatic functionalities to a greater extent of fused aromatic structures characteristic of mature chars.

The NMR spectra give some evidence for the possible trapping of tar in the char. When peaks attributable to spinning side bands are discounted, there is no evidence for aliphatic components in the chars formed at atmospheric pressure and at 6 bar. However, as the pressure is further increased a peak becomes evident at ca 35 ppm, and that peak is greater at 26 bar. This can be regarded as evidence for aliphatic structures trapped in the tar materials in the char.

4. Conclusion

The results presented prove that pressure has an influence on the quality of the pyrolysis products. However it has no influence on the quantity of the products from slow pyrolysis. The water content in bio-oil limits the usefulness of the bio-oil as a fuel. The bio-oil contains very high levels of various phenol derivatives. These can be further processed to provide valuable products.

Table 2

<table>
<thead>
<tr>
<th>Material and pressure</th>
<th>Elemental composition, wt.%</th>
<th>HHV Eq. (1) MJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Raw MxG</td>
<td>46.6</td>
<td>6.4</td>
</tr>
<tr>
<td>MxG char at atm</td>
<td>86.4</td>
<td>2.7</td>
</tr>
<tr>
<td>MxG char at 6 bar</td>
<td>89.2</td>
<td>3.25</td>
</tr>
<tr>
<td>MxG char at 11 bar</td>
<td>90.0</td>
<td>2.26</td>
</tr>
<tr>
<td>MxG char at 16 bar</td>
<td>93.2</td>
<td>1.66</td>
</tr>
<tr>
<td>M char at 21 bar</td>
<td>91.8</td>
<td>2.63</td>
</tr>
<tr>
<td>M char at 26 bar</td>
<td>87.6</td>
<td>3.65</td>
</tr>
</tbody>
</table>
As pressure is increased the surface area is decreased, because
the pores become clogged with trapped tar, and these also collapse.
The NMR spectra indicate that chars formed at the higher pres-
sures have more extended fused aromatic structures, reflected also
in the higher carbon contents, than those formed at the lower
pressures.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in

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