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1 **Microwave and Slow Pyrolysis Biochar – Comparison of Physical and Functional** 2 **Properties**

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9 Keywords: biochar, microwave, pyrolysis, torrefaction, stability

10 **Abstract**

11 This paper reports work that compares slow pyrolysis and MW pyrolysis of two different
12 feedstock (willow chips and straw), with particular focus on physical properties of resulting
13 chars and their relation to biochar soil function. In these experiments, slow pyrolysis
14 laboratory units at the University of Edinburgh and the MW pyrolysis units at the University of
15 York were used to produce biochar from identical feedstock under a range of temperatures.
16 Physical properties and stability of thus produced biochar from both systems were then
17 analysed and compared.

18 The results showed that using MW, pyrolysis can occur even at temperatures of around
19 200 °C, while in case of conventional heating a higher temperature and residence time was
20 required to obtain similar results. This paper presents new data not only on the comparison
21 of biochar from microwave and slow pyrolysis in terms of physical properties, but also in
22 respect to their carbon sequestration potential, i.e. stability.

23 **1 Introduction**

24 Biochar is a carbon-rich solid product of thermal stabilisation of organic matter created for
25 safe and potentially beneficial storage in soil. It differs from other solid products of
26 thermochemical conversion in that long-term carbon storage is the primary objective, rather
27 than creation of feedstock for processing industries or fuels such as charcoal, coke and
28 activated carbon. Due to this distinct function, and often a combination of several functions,
29 e.g. soil improvement or remediation, the requirements on biochar are different to those
30 other uses of solid carbonaceous residues. In particular it is necessary to ensure that

31 biochar produced from a particular feedstock by any given technology is at least
32 environmentally benign, or even has positive effects (e.g., on plant growth, soil structure,
33 water management etc.). The current state-of-the-art knowledge on biochar and its
34 interaction with the environment has recently been reviewed by Sohi et al. [1] and Lehmann
35 and Joseph [2]. In addition to its environmental impact, biochar must also be highly stable to
36 ensure long-term carbon sequestration. The global potential for sustainable global biochar
37 deployment has been recently analysed by Woolf et al. [3], and the potential benefits and
38 risks of biochar were assessed in a report to the UK Department of Energy and Climate
39 Change (DECC) [4]. This report, besides analysing the potential for biochar deployment in
40 the UK also discusses benefits and issues of biochar deployment. It particularly highlights
41 the need to better understand the economics of “pyrolysis biochar systems” (PBS) and the
42 long term stability of biochar.

43 The distinctly new use of the material (biochar) presents a number of requirements and
44 challenges that are different from its other (more traditional) uses, such as combustion or
45 activated carbon. As a result, new, or modified traditional thermochemical processes are
46 being proposed that target the specifics of biochar production. This offers the opportunity to
47 produce and test a wide range of biochar and assess its suitability for application under
48 different environmental, economic and agricultural scenarios. Yet, to date there are only very
49 few studies attempting to compare biochar produced from the same feedstock by alternative
50 technologies [5], [6]. This is why we decided to study and compare biochar produced by a
51 novel technology of low temperature microwave (MW) pyrolysis with biochar produced under
52 similar thermal regime by slow pyrolysis (relatively established technology suitable for
53 biochar production).

54 Microwave heating offers several advantages over conventional heating, as it is often more
55 controllable [7], [8] energy [9–11] and cost [12] efficient and therefore in many cases may
56 offer a potentially attractive alternative to “conventional” pyrolysis systems. Microwave
57 processing has been shown to be effective at both pilot scale [13] and at industrial scale for

58 the production of plant material extracts of outstanding stability and purity [14]. Efficiency of
59 microwave treatment for pyrolysis of biomass has been proved in a number of publications
60 [15–17]. Furthermore, several researchers looked at comparing MW pyrolysis with
61 conventional pyrolysis and identified considerable differences between the two methods [18–
62 20]. These papers emphasise the key differences between the different pyrolysis methods
63 as being temperature of decomposition, heating rates and requirement for feedstock pre-
64 processing (e.g. shredding or drying). However, only few studies looked at MW biochar
65 production [21], [22] and to our best knowledge, direct comparison of bio-char properties
66 obtained by conventional pyrolysis and MW pyrolysis have never been reported.

67 In this study we focussed on low temperature thermochemical conversion (up to 350°C), as
68 this is the operating range of the new promising low temperature MW pyrolysis technology
69 and we compared the solid products with those produced by slow pyrolysis/ torrefaction in
70 the same temperature range. This paper presents results from our experimental
71 investigation of the impact of production conditions, i.e. pyrolysis temperature and heating
72 method on the biochar product, its properties and stability.

73 **2 Materials and methods**

74 **2.1 Materials**

75 The raw materials used in our experiments were willow wood chips (WC), supplied by
76 Renewable Energy Suppliers Ltd (Koolfuel 15), and mixed straw pellets (StP) consisting of
77 equal portions of wheat and rape straw, supplied by Straw Pellets Ltd. The properties of the
78 feedstock are shown in

79 Table 1. The feedstock was used as received, without any additional pre-processing.

80 2.2 Experimental apparatus and procedure

81 2.2.1 Slow pyrolysis/ Torrefaction using conventional heating

82 The slow pyrolysis apparatus used, as shown in Figure 1, was a fixed-bed reactor
83 comprising a quartz glass reactor tube (50mm i/d) with a sintered glass plate at the base.

84 The reactor tube was heated by a 12kW infrared image furnace (ULVAC RHL-P610C) with
85 temperature control based on a thermocouple immersed within the test sample. Inert gas
86 (nitrogen) is supplied at a controlled rate and, after preheating in the bottom part of the
87 reactor, it passed up through the sample carrying volatiles and syngas into a condenser train.

88 The train consisted of two parts; first the gas passed through a heated filter (170 ± 15 °C)
89 where any entrained particulates were separated, as well as some heavy tars. Second, the
90 particulate-free gas passed through an air condenser with ambient-temperature receiver and
91 two cold traps maintained at -50 to -30 °C using liquid nitrogen-cooled acetone. The
92 composition of the non-condensable gases leaving the second trap was continuously
93 monitored using an online quadrupole mass spectrometer (Hiden HPR-20 QIC, Hiden
94 Analytical Ltd.). The gases were collected in a series of gas bags (Cali-5-Bond™ and SKC
95 flex-foil) for offline analysis at the end of the run. The volume of gas collected was
96 determined by passing it through a volumetric gas flow meter (Ritter, TG5). Differential
97 pressure over the sample bed and gauge pressure at the reactor head were also monitored.

98 In a typical slow pyrolysis experiment a biomass sample (approx. 50g) was charged to the
99 reactor tube before assembling the apparatus. Pressure sensors were zeroed and the
100 reactor was purged with nitrogen before establishing a steady flow rate of nitrogen as carrier
101 gas; an inlet flow of 0.33 l min^{-1} was used giving a calculated linear cold flow velocity within
102 the empty reactor tube of 3 mm s^{-1} .

103 The sample was heated at an average heating rate of 5 °C min^{-1} to the required hold
104 temperature (200, 250, 300 and 350 °C). The hold temperature was maintained for 10

105 minutes before the heating was stopped and the sample cooled under nitrogen (rapid cooling
106 ensured by built in water cooling of the furnace).

107 Throughout each experiment sample temperature, reactor pressure and differential pressure
108 were monitored and logged. Product yields are given as recovered yields expressed as
109 percent by weight of dry feed. Not all solid and liquid products could be recovered from the
110 apparatus; handling losses were estimated at 5-10% in total

111 2.2.2 Microwave pyrolysis

112 The MW treatment of biomass was carried out using a Milestone ROTO SYNTH Rotative
113 Solid Phase Microwave Reactor (Milestone Srl., Italy) fitted with a VAC 2000 vacuum
114 module in series. Samples were exposed to a maximum MW power of 1200W with an
115 operating microwave frequency of 2.45 GHz (wavelength 12.2 cm). Samples of wood chips
116 (ca. 130g) and straw pellets (ca. 175g) were placed in a 2L glass flask within the microwave
117 cavity (see Figure 2). MW pyrolysis was carried out under constant MW power (1200W) and
118 vacuum (initial pressure ca. 30 mbar and increasing up to 0.3 bar at the maximum heating
119 rate temperature point). In a preliminary experiment microwave pyrolysis of biomass was
120 carried out under the flow of nitrogen at atmospheric pressure, however, under these
121 conditions significant amounts of bio-oil condensed and then polymerised within the sample
122 vessel. Results from this set of tests showed that the yield of char and its characteristics
123 obtained both under low vacuum and under flow of nitrogen were very similar and therefor
124 further experiments were carried out under vacuum, to avoid condensation issues. Due to
125 differences in MW irradiation absorption efficiency, biochar (and co-products) from WC and
126 StP were obtained at different temperatures (170 °C and 200 °C respectively). Monitoring of
127 the process was carried out by measuring temperature using two different methods;
128 temperature of volatile fractions was measured by thermocouple on the exit tube, and that of
129 solid material was measured by infrared detector within the MW cavity (see Figure 2). The
130 sample temperatures were found to be within 15 °C indicating good correlation of
131 temperature measurement. Due to the instantaneous evaporation of the newly formed bio-oil,

132 the heat of evaporation retarded potential overheating at pyrolysis centres, whilst the vapour
133 heated the bulk of the solid as it diffused out from the pyrolysis centre [23]. At temperatures
134 below 70°C physisorbed water was collected; with increasing temperature chemisorbed
135 water was observed around 110-120°C and finally at temperatures between 130 and 160°C
136 non-compressible gases and bio-oil were observed. The process pressure was monitored at
137 all times. Liquid fractions were collected via the water-cooled vacuum trap, which collected
138 and condensed vapours produced during the process.

139 2.3 Characterisation of products

140 2.4 FTIR

141 Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectra were recorded
142 on a Bruker EQUINOX-55 instrument equipped with a liquid N₂ cooled MCT detector. 64
143 scans, 2 cm⁻¹ resolution was used.

144 2.4.1 True density

145 The true density of biochar was determined using a helium pycnometer (Ultrapyc 1200e,
146 Quantachrome Instruments). For these tests, approximately 8 cm³ of biochar (as produced)
147 per test was used. The measurement procedure included repeated flushing (purging) of the
148 sample cell with helium followed by repeated measurements (typically 20) until a satisfactory
149 standard deviation value was achieved.

150 2.4.2 Porosity

151 Biochar porosity was determined by mercury porosimetry using a Quantochrome
152 Poremaster 90 at the University of Strathclyde. The measurements were done in two stages
153 and the combined data were used to calculate pore size, volume etc. The stage 1 analysis
154 was conducted in the pressure range of ~0-345 kPa (50 psi) and the stage 2 analysis was
155 conducted at pressure up to 413.7 MPa (60,000 psi).

156 2.4.3 Elemental analysis

157 The CHN content of biomass and biochar samples was determined using an Exeter CE440
158 Elemental Analyser.

159 2.4.4 Stability

160 The carbon contained in biochar can be classified into several fractions depending on its
161 stability, i.e. resistance to environmental degradation. The stable carbon fraction was
162 determined for all biochar using an accelerated ageing assay. This assay involved thermal
163 and chemical oxidation of milled biochar samples. Accelerated ageing using oxidation was
164 used given that degradation of biochar in soils is a typically oxidative process. Samples were
165 placed in 5% hydrogen peroxide and heated to 80 °C, and carbon stability then was
166 calculated gravimetrically using the %C data of samples before and after oxidation.

167 2.4.5 Thermogravimetric analysis

168 Thermogravimetric analysis (TG) was performed using a Netzsch STA 409 at scan rates of
169 10 °C min⁻¹, with typically 80 mg sample under flowing N₂ at 100 mL min⁻¹.

170 3 Results and discussion

171 3.1 Product yields

172 The main objective of this work was to compare the differences between MW and
173 conventional slow pyrolysis in terms of product yields and their properties, with focus on the
174 solid products (biochar). From the yield data shown in Table 2 it is immediately obvious that
175 the distribution of products from MW pyrolysis is considerably different to that from slow
176 pyrolysis. Despite the low pyrolysis temperature, MW preferentially generated liquids and
177 gases, yielding only 33.7wt% and 27.3 wt.% of biochar for StP and WC respectively. In the
178 temperature range deployed, slow pyrolysis on the other hand yielded mostly solid products,
179 with yields decreasing with increasing temperature. The yields of MW biochar are
180 considerably lower compared to those obtained by slow pyrolysis in similar temperature
181 range or even at over 150 °C higher temperature. Similar results have been reported in
182 the literature [18] and attributed to the activation of amorphous cellulose under MW
183 irradiation.

184 3.2 Biochar characteristics

185 3.2.1 FT-IR

186 The considerable differences in yields between MW and slow pyrolysis suggest that the
187 characteristics of the resulting biochar will also differ. We used ATR- FTIR spectroscopy to
188 assess the progress of biomass conversion and to identify whether there were any
189 similarities between the MW and slow pyrolysis biochar. Dramatic changes in FTIR spectra
190 of biochar derived from WC during conventional heating take place at temperatures above
191 250°C (see Figure 3 A), where the process of decomposition of cellulose becomes more
192 significant and the cellulose band in the FTIR spectra (peak at 1030 cm⁻¹) is dramatically
193 reduced in comparison with the peak at 1604 cm⁻¹ representing the lignin aromatic system
194 (see Figure 3 B). The peak at 1705 cm⁻¹ corresponds to the cellulose aldehyde group
195 therefore further emphasising the cellulose decomposition.

196 FTIR spectra of biochar obtained by microwave pyrolysis at 170°C and conventional heating
197 at 350°C appear largely similar (see Figure 3 A). Furthermore, the exponential
198 approximation of lignin-to-cellulose ratios (measured as $A_{1600}^{-1}/A_{1030}^{-1}$) obtained under
199 slow pyrolysis at different temperatures (solid line in Figure 3B) showed that properties of a
200 microwave obtained sample (170°C) were very similar to the slow pyrolysis sample which
201 could be obtained at temperature of approx. 330°C (see Figure 3 B). Therefore to achieve
202 the same composition of a wood biochar sample the microwave process requires a
203 temperature which is 160°C less than that needed in the slow pyrolysis process. The
204 additional peak at 1317 cm⁻¹ in Figure 3 A (corresponding to deformation vibration of
205 CH₂-C bond) [24] is indicative of MW pyrolysis operating in a different manner to slow
206 pyrolysis.

207 The same trends are seen for StP shown in Figure 4 with an increased impact of lignin. The
208 results show again that to achieve the same composition of a straw biochar sample the
209 microwave process requires a temperature which is 157°C less than that needed in the slow
210 pyrolysis process (see Figure 4 B).

211 3.2.2 Thermo-Gravimetric Analysis (TGA)

212 To both further assess the extent of conversion of the original material under the different
213 pyrolysis conditions and to quantitatively analyse the remaining biomass composition TGA
214 analysis was used. Figure 5 shows an example of the TG analysis applied to wood chips to
215 estimate composition, based on work of Carrie et al. [23].

216 As can be seen in the trace, water content for WC was approximately 9%, cellulose 40%,
217 hemi-cellulose 38% and lignin 25%, which is in good correlation with literature data for the
218 relative composition of wood based on TG analysis [24]. The 9% water content is likely to
219 be responsible for the highly efficient microwave absorption observed during microwave
220 pyrolysis of wood chips.

221 The TG data for all WC derived biochar samples is shown in Figure 6A; the data falls into
222 two groups. The first group, with a TG trace similar to the original material and therefore a
223 similar structural component composition, are samples prepared below 250°C using
224 conventional heating. The second group, with lower mass loss at high temperatures, are
225 samples prepared at 300°C and 350°C by conventional heating and the microwave sample
226 prepared at 170°C. These samples have reduced volatile carbon content – through
227 decomposition of hemicellulose and cellulose. Figure 6B shows the relative cellulose
228 content for the various bio-chars. The chart shows a small rise in relative cellulose content
229 between feedstock and slow pyrolysis samples prepared between 200°C and 250°C; this is
230 due to decomposition of hemi-cellulose increasing the relative cellulose content. Above this
231 temperature for slow pyrolysis samples there is a dramatic change caused by decomposition
232 of cellulose at the elevated temperatures. MW pyrolysis prepared bio-chars (170°C) have
233 similar cellulose content to that of higher temperature slow pyrolysis biochar; this shows that
234 microwave irradiation decomposes cellulose at lower temperatures than conventional
235 heating for this feedstock. Comparing cellulose content of samples prepared by SP and MW
236 pyrolysis shows a ~160°C difference between preparation methods, which is in good
237 correlation with data previously observed by FT-IR (See Figure 3)

238 Data for straw pellet biochar is shown in Figure 7, a similar trend to that observed in WC
239 biochar can be clearly observed. Two clear behaviour groups were present in the TGA
240 trace, one with low cellulose content formed at higher temperatures of preparation and by
241 MW pyrolysis and one with higher cellulose content from lower temperature slow pyrolysis
242 preparations (<300°C). The different decomposition patterns of WC and StP biochar were
243 most likely due to the difference in composition of the starting material (see Table 1).

244 3.2.3 Porosity and true density of biochar

245 The physical properties of biochar have been assessed, as measures of the degree of
246 conversion, based on porosity and true density. The true density values for the different
247 chars are shown in Figure 8. It can be seen that the two materials show somewhat different
248 trends. In case of WC the true density initially increased with temperature between 200 and
249 250 °C, followed by gradual decrease with further temperature increase up to 350 °C. On the
250 other hand, straw pellets showed gradual decrease of true density with increasing peak
251 treatment temperature. Comparing the true density values for the MW pyrolysis char with
252 those produced by conventional heating, it can be seen that StP (MW) produced at 200 °C
253 has a true density comparable to that of StP 200, i.e. close to that of the starting material. In
254 contrast, WC (MW) has a density in the range of WC 250 and WC 300, i.e. showing some
255 structural development compared to the starting material.

256 To gain further insight into structural changes of the two biomass feedstock as a result of
257 MW or conventional heating, the porosity of the samples was assessed. The data in Table 3
258 show that both surface area and pore volume are a function of temperature, with the lowest
259 value at 200 °C and highest value at 350 °C (in the temperature range used). For both
260 feedstock, the data show that MW pyrolysis considerably promotes porosity development, as
261 both the surface area and pore volume were considerably higher for materials prepared by
262 MW pyrolysis than for those prepared by conventional heating at comparable temperature.
263 This was particularly evident in case of WC, where the surface area of WC (MW) was as
264 high as 14 m²/g, i.e. more than three times higher than that of WC 200, and nearly two times

265 higher than that of WC 350. The reason for such relatively high porosity of MW chars even at
266 these low temperatures is most likely the different heat and mass transfer mechanism during
267 MW heating. As MW heating is a volumetric heating without any clear high temperature front,
268 the volatiles formed within the particle can escape more freely. As release of volatiles is the
269 main mechanism responsible for porosity development at temperatures below 500 °C [25],
270 the improved release of volatiles during MW pyrolysis results in higher porosity. In addition,
271 due to the absence of a thermal front and the overall relatively low temperatures during MW
272 treatment used in this work, the extent of secondary reactions that could cause formation of
273 deposits and thus pore blockages was minimised.

274 3.2.4 Carbon content, yield and stability

275 One of the main features of biochar is its potential to stabilise carbon that is removed from
276 the atmosphere by plants by photosynthesis and stored in cell walls during their growth, and
277 therefore the amount of carbon contained in biochar, and the stability of this carbon is of high
278 importance. Table 4 shows the concentration of carbon in char produced at different
279 temperatures, as well as the yield of char at respective temperatures. There is a clear
280 increasing trend in carbon content with temperature and a decreasing char yield. As a result,
281 the carbon yield decreased with temperature from nearly 100% in case of WC 200 and StP
282 200 down to just around 60% for chars prepared at 350 °C. In comparison to slow pyrolysis,
283 MW pyrolysis showed considerably lower char yield and consequently higher char carbon
284 content. The carbon yield for both MW chars was also lower than for any of the slow
285 pyrolysis chars, only around 40%.

286 Table 4 also shows results of carbon stability measured by accelerated aging (using
287 enhanced oxidation) and it can be seen that the overall trend is different and perhaps less
288 clear. It can be seen that the relative stability does not change much with temperature up to
289 at least 300 °C, and the stability remains at comparable level to that of the starting material
290 (not shown). This is not unexpected, as the degree of charring (conversion) achieved under
291 the conditions used (slow pyrolysis) was minimal. In case of chars produced at higher

292 temperatures the stability clearly increases with temperature and can reach well over 95%
293 [26]. As a result of the decreasing carbon yield and only moderate increase of its stability,
294 the yield of stable carbon is slightly decreased with temperature, although the decrease was
295 not very significant and the yield stabilised at around 30 %C for StP chars and at around
296 35 %C for WC chars.

297 MW chars on the other hand show relatively high stability, comparable to higher temperature
298 slow pyrolysis chars. This is most likely due to the considerably higher degree of conversion
299 achieved by MW heating, as evidenced by other data shown in this work (e.g. FT-IR, TGA,
300 porosity etc.). Nevertheless, due to the low carbon yields of MW biochar the yields of stable
301 carbon are low (around 21-25 %C) when compared to slow pyrolysis chars. This means that
302 although MW pyrolysis conducted at very low temperatures (170-200 °C) produces chars
303 with stability considerably higher than that of the starting material or even materials
304 produced by slow pyrolysis at comparable temperatures, the overall carbon sequestration
305 potential of this technology is limited by the low yield of stable carbon.

306 **4 Conclusions**

307 This work provided some new insights into the differences between biochar produced by
308 microwave heating and conventional heating at low temperatures. For both feedstock, it is
309 clear that only minimum transformation occurred in case of slow pyrolysis at temperatures
310 below 300°C, with only some signs of conversion of hemicellulose. MW biochar on the other
311 hand showed considerable degree of transformation, as evidenced by the higher
312 decomposition temperature and slow decomposition rate in TGA analysis. It can be seen,
313 that in case of straw pellets, even char produced at 350 °C showed a lower degree of
314 volatiles release than the MW biochar. In case of WC, biochar produced at 300 and 350°C
315 exhibited a comparable decomposition pattern to that MW biochar and thus it can be
316 concluded that the material achieved similar levels of conversion. The higher degree of
317 conversion of MW biochar was also reflected in its stability, as MW biochar showed
318 comparable or higher stability than chars produced by slow pyrolysis at 300-350 °C, at least

319 in case of woody biomass. However, due to the significantly lower yields of char from MW
320 pyrolysis, the carbon sequestration potential of the technology is limited and lower than that
321 of slow pyrolysis, at least in the temperature ranges investigated. This apparent shortfall in
322 carbon sequestration potential of MW pyrolysis is however likely to be offset by its high
323 potential for production of renewable energy and materials, and a detailed LCA study would
324 be needed to fully compare the two technologies.

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408 Figure 1 - Laboratory batch pyrolysis unit at The University of Edinburgh
409 Figure 2 - Microwave pyrolysis setup at The University of York
410 Figure 3 – A) ATR-FTIR spectrum of willow chips derived biochar. B) Lignin-cellulose ratio
411 as a function of pyrolysis temperature.
412 Figure 4 - A) ATR-FTIR spectrum of straw pellets derived biochar. B) Lignin-cellulose ratio
413 as a function of pyrolysis temperature.
414 Figure 5 - Example of structural components analysis based on TG analysis of wood chips.
415 Figure 6 - A) Comparison of TG curves of WC biochars produced by MW pyrolysis and slow
416 pyrolysis methods. B) Influence sample preparation temperature on cellulose content within
417 wood chips samples.
418 Figure 7 - A) Comparison of TG curves of StP biochars produced by MW pyrolysis and slow
419 pyrolysis methods. B) Influence sample preparation temperature on cellulose content within
420 straw pellets samples.
421 Figure 8 - True density of feedstock and char as a function of production conditions
422

- 423 Table 1 - Biomass feedstock composition
- 424 Table 2 – Pyrolysis product yields
- 425 Table 3 - Feedstock and biochar porosity, as determined by BET and Hg porosimetry
- 426 Table 4 - Char yield, carbon content, stability and stable carbon yield
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