Microwave and Slow Pyrolysis Biochar – Comparison of Physical and Functional Properties

Microwave and Slow Pyrolysis Biochar – Comparison of Physical and Functional Properties

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Abstract

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

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

1 Introduction

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

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

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

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

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

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

2 Materials and methods

2.1 Materials

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

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

2.2 Experimental apparatus and procedure

2.2.1 Slow pyrolysis/ Torrefaction using conventional heating

The slow pyrolysis apparatus used, as shown in Figure 1, was a fixed-bed reactor comprising a quartz glass reactor tube (50mm i/d) with a sintered glass plate at the base. The reactor tube was heated by a 12kW infrared image furnace (ULVAC RHL-P610C) with temperature control based on a thermocouple immersed within the test sample. Inert gas (nitrogen) is supplied at a controlled rate and, after preheating in the bottom part of the reactor, it passed up through the sample carrying volatiles and syngas into a condenser train.

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

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

The sample was heated at an average heating rate of 5 ℃ min^{-1} to the required hold temperature (200, 250, 300 and 350 ℃). 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℃ and 200℃ 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 ^{o}C indicating good correlation of
131 temperature measurement. Due to the instantaneous evaporation of the newly formed bio-oil,

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

2.3 Characterisation of products

2.4 FTIR

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectra were recorded on a Bruker EQUINOX-55 instrument equipped with a liquid N_2 cooled MCT detector. 64 scans, 2 cm^{-1} resolution was used.

2.4.1 True density

The true density of biochar was determined using a helium pycnometer (Ultrapyc 1200e, Quantachrome Instruments). For these tests, approximately 8 cm^3 of biochar (as produced) per test was used. The measurement procedure included repeated flushing (purging) of the sample cell with helium followed by repeated measurements (typically 20) until a satisfactory standard deviation value was achieved.

2.4.2 Porosity

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

2.4.3 Elemental analysis

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

2.4.4 Stability

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

2.4.5 Thermogravimetric analysis

Thermogravimetric analysis (TG was performed using a Netzsch STA 409 at scan rates of 10°C min^{-1}, with typically 80 mg sample under flowing N_2 at 100 mL min^{-1}.

3 Results and discussion

3.1 Product yields

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

3.2 Biochar characteristics

3.2.1 FT-IR

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

FTIR spectra of biochar obtained by microwave pyrolysis at 170℃ and conventional heating at 350℃ appear largely similar (see Figure 3 A). Furthermore, the exponential approximation of lignin-to-cellulose ratios (measured as $A1600^{-1}/A1030^{-1}$) obtained under slow pyrolysis at different temperatures (solid line in Figure 3B) showed that properties of a microwave obtained sample (170℃) were very similar to the slow pyrolysis sample which could be obtained at temperature of approx. 330℃ (see Figure 3 B). Therefore to achieve the same composition of a wood biochar sample the microwave process requires a temperature which is 160℃ less than that needed in the slow pyrolysis process. The additional peak at 1317 cm^{-1} in Figure 3 A (corresponding to deformation vibration of CH_2-C bond) [24] is indicative of MW pyrolysis operating in a different manner to slow pyrolysis.

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

3.2.2 Thermo-Gravimetric Analysis (TGA)

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

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

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

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

3.2.3 Porosity and true density of biochar

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

To gain further insight into structural changes of the two biomass feedstock as a result of MW or conventional heating, the porosity of the samples was assessed. The data in Table 3 show that both surface area and pore volume are a function of temperature, with the lowest value at 200 ℃ and highest value at 350 ℃ (in the temperature range used). For both feedstock, the data show that MW pyrolysis considerably promotes porosity development, as both the surface area and pore volume were considerably higher for materials prepared by MW pyrolysis than for those prepared by conventional heating at comparable temperature. This was particularly evident in case of WC, where the surface area of WC (MW) was as high as 14 m^2/g, i.e. more than three times higher than that of WC 200, and nearly two times

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

3.2.4 Carbon content, yield and stability

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

Table 4 also shows results of carbon stability measured by accelerated aging (using enhanced oxidation) and it can be seen that the overall trend is different and perhaps less clear. It can be seen that the relative stability does not change much with temperature up to at least 300 ℃, and the stability remains at comparable level to that of the starting material (not shown). This is not unexpected, as the degree of charring (conversion) achieved under 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

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

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Figure 1 - Laboratory batch pyrolysis unit at The University of Edinburgh

Figure 2 - Microwave pyrolysis setup at The University of York

Figure 3 – A) ATR-FTIR spectrum of willow chips derived biochar. B) Lignin-cellulose ratio as a function of pyrolysis temperature.

Figure 4 - A) ATR-FTIR spectrum of straw pellets derived biochar. B) Lignin-cellulose ratio as a function of pyrolysis temperature.

Figure 5 - Example of structural components analysis based on TG analysis of wood chips.

Figure 6 - A) Comparison of TG curves of WC biochars produced by MW pyrolysis and slow pyrolysis methods. B) Influence sample preparation temperature on cellulose content within wood chips samples.

Figure 7 - A) Comparison of TG curves of StP biochars produced by MW pyrolysis and slow pyrolysis methods. B) Influence sample preparation temperature on cellulose content within straw pellets samples.

Figure 8 - True density of feedstock and char as a function of production conditions

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