

THE UNIVERSITY of EDINBURGH

Edinburgh Research Explorer

The effect of pyrolysis conditions on biochar stability as determined by three methods

Citation for published version:

Crombie, K, Masek, O, Sohi, SP, Brownsort, P & Cross, A 2013, 'The effect of pyrolysis conditions on biochar stability as determined by three methods', GCB Bioenergy, vol. 5, no. 2, pp. 122-131. https://doi.org/10.1111/gcbb.12030

Digital Object Identifier (DOI):

10.1111/gcbb.12030

Link: Link to publication record in Edinburgh Research Explorer

Document Version: Early version, also known as pre-print

Published In: GCB Bioenergy

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



1	THE EFFECT OF PYROLYSIS CONDITIONS ON BIOCHAR
2	STABILITY AS DETERMINED BY THREE METHODS
3	Running Title - Crombie et al.: Assessing biochar stability
4	
5	KYLE CROMBIE, ONDŘEJ MAŠEK*, SARAN P. SOHI, PETER BROWNSORT AND
6	ANDREW CROSS
7	
8	
9	
10	
11	UK Biochar Research Centre, School of GeoSciences, University of Edinburgh,
12	Crew Building, King's Buildings, Edinburgh EH9 3JN, UK
13	Tel. 0131 6505095 Email: <u>kncrombie@gmail.com</u> , <u>ondrej.masek@ed.ac.uk</u>
14	
15	
16	
17	Keywords: Biochar, carbon sequestration, pyrolysis, stability determination, Edinburgh
18	toolkit, Stable carbon, physiochemical properties
19	
20	
21	
22	
23	
24	Primary Research Article
25	

26 Abstract

27 Biochar is the porous, carbonaceous material produced by thermo-chemical treatment of organic materials in an oxygen-limited environment. In general, most biochar can be 28 29 considered resistant to chemical and biological decomposition, and therefore suitable for carbon (C) sequestration. However, to assess the C sequestration potential of different types 30 31 of biochar, a reliable determination of their stability is needed. Several techniques for assessing biochar stability have been proposed, e.g. proximate analysis, oxygen (O): C ratio 32 and hydrogen (H): C ratio, however, none of them are yet widely recognised nor validated for 33 34 this purpose. Biochar produced from three feedstocks (Pine, Rice husk and Wheat straw) at four temperatures (350, 450, 550, 650°C) and two heating rates (5 and 100°C/min) was 35 analysed using three methods of stability determination: proximate analysis, ultimate analysis 36 37 and a new analytical tool developed at the UK Biochar Research Centre known as the Edinburgh accelerated aging tool (Edinburgh stability tool). As expected, increased pyrolysis 38 temperatures resulted in higher fractions of stable C and total C due to an increased release of 39 40 volatiles. Data from the Edinburgh stability tool was compared with those obtained by the other methods, i.e. fixed C, volatile matter, O:C and H:C ratio, to investigate potential 41 relationships between them. Results of this comparison showed that there was a strong 42 correlation (R > 0.79) between the stable C determined by the Edinburgh stability tool and 43 fixed C, volatile matter and O:C, however H:C showed a weaker correlation (R = 0.65). An 44 45 understanding of the influence of feedstock and production conditions on the long term stability of biochar is pivotal for its function as a C mitigation measure, as production and use 46 of unstable biochar would result in a relatively rapid return of C into the atmosphere, thus 47 48 potentially intensifying climate change rather than alleviating it.

49

51 Introduction

Biochar is the C-rich solid produced by thermo-chemical conversion (pyrolysis) of 52 biomass in an oxygen depleted environment for the purpose of soil amendment. Biomass 53 pyrolysis diverts C away from the dynamic atmosphere–biosphere pool and into a far more 54 55 stable pool decomposing at a much slower rate than its parent feedstock (Preston & Schmidt 2006; Liang *et al.* 2008; Spokas 2010), avoiding the complete return to the air of CO₂ from 56 natural decay or burning. Producing biochar and incorporating it into soil for the purpose of 57 soil improvement is thus one proposed method to increase long term storage of C in the 58 59 biosphere (Shackley et al. 2009; Sohi et al. 2010). As a relatively complex proposition that concerns energy production as well as C sequestration and soil management, it is the subject 60 of increasing multi-disciplinary research. 61

It is known that the physiochemical properties of biochar depend on the starting organic material, the carbonization system used to make it and selected production parameters (Enders *et al.* 2012). These properties then define the functional properties such as biochar soil stability which is essential to demonstrating the longevity of stored C and therefore establish an effective means for C abatement.

Biochar can be considered part of the black C continuum, a term used to describe the 67 by-products of combustion that also includes – in order of increasing stability – charcoal, 68 coal, soot and graphite (Masiello 2004; Baldock & Smernik 2002; Liang et al. 2008). 69 Through the use of C-14 dating, black C has been found to be the oldest fraction of C in soils, 70 with the most stable components displaying mean residence times of several thousand years 71 72 (Lehmann et al. 2009; Liang et al. 2008; Preston & Schmidt 2006). The complexity and chemical heterogeneity of black C has made it difficult to establish a single method suited to 73 assessing the potential stability of all materials in the continuum (Hammes et al. 2006) and 74 hence, there is no globally-established method for determination of absolute stability for 75

⁷⁶ black C or biochar. However, a number of methods for comparing the relative stability of
⁷⁷ different biochar materials have emerged. These include proximate analysis (ASTM D1762⁷⁸ 84; Antal & Gronil 2003), O:C or H:C molar ratios (Spokas 2010; Enders *et al.* 2012; IBI
⁷⁹ Guidelines 2012), and chemical oxidation (Cross & Sohi 2012).

Proximate analysis has long been used to assess the quality of coal and charcoal fuels, 80 defining moisture, "volatile matter", "fixed C" and ash. Proximate analysis requires high 81 temperatures (900°C for determination of volatile matter and 750°C for ash determination) for 82 extended periods of time, this has practical drawbacks and can lead to an inflated estimate of 83 84 fixed C by underestimation of ash content (Masiello 2004; Downie et al. 2009; Enders et al. 2012). Furthermore, proximate analysis relies on thermal decomposition for calculation of 85 products, which does not provide an analogue for the degradative (primarily oxidative) 86 processes that exist in soil. 87

Pyrolysis favours the elimination of H and O over C, such that extending pyrolysis 88 reactions results in a solid residue (char) of progressively higher C concentration. The utility 89 of elemental ratios, provided by ultimate analysis, as indicators of biochar stability has been 90 extensively researched (Kuhlbusch 1995; Hedges et al. 2000; Masiello 2004; Spokas 2010; 91 92 IBI Guidelines 2012; Schmidt et al. 2012). The O:C ratios assigned to materials encompassed by the black C continuum showed a systematic increase from 0 for graphite to >0.6 for 93 94 material not considered to be black C. For aged biochar samples, changes in O:C ratio at the 95 surface indicates the extent to which they have been oxidised by their environment (Cheng et 96 al 2006). For newly produced samples, O:C indicates the progression of deoxygenation 97 which can serve as a proxy for the extent of charring. Correlation of O:C with the mean 98 residence time of various biochar samples in soil, extrapolated from various short-term 99 incubation experiments confirmed a general, inverse relationship between this ratio and biochar stability (Spokas 2010). This work proposed that biochar displaying an O:C ratio 100

>0.6 would be closer to biomass composition than to graphite and would have a mean
residence time <100 years. Conversely, material with an O:C ratio in the range 0.2–0.6 would
be expected to have mean residence time of 100–1000 years. To avoid confounding analyses
with non-black C species IBI guidelines for quantifying O:C ratio recommend the application
of an acid treatment for the removal of carbonates and determination of organic C (IBI
Guidelines 2012).

107 The ratio of H:C has also been proposed as an index of aromaticity and resistance of char to microbial and chemical degradation (Kuhlbusch 1995; Kuhlbusch & Crutzen 1995). 108 As with O:C quantification, pre-treatment steps (acid and thermal treatment) can be applied 109 to remove inorganic and organic C prior to total H and C determination. Kuhlbusch (1995) 110 also described the use of a correction factor to exclude H bound to elements other than C, 111 most likely silicate and therefore generating an H:C ratio only for the stable fraction of char. 112 However, Enders et al (2012) showed that their results ranked poultry manure, based on H:C 113 ratio, to have equal stability to woody samples which were found to be much more stable thus 114 creating doubt over the suitability of H:C as a method of stability determination. 115 In order for the potential of biochar for C sequestration and agricultural benefit to be 116 117 fully realised, it is necessary that the different functional characteristics of biochar such as stability can be rapidly assessed prior to deployment. The method put forward by Cross and 118 119 Sohi (Cross & Sohi 2012) establishes an approach that directly quantifies stability by 120 eliminating the less stable portion of material by oxidation. Controlled but fast addition of 121 hydrogen peroxide (H_2O_2) is used as an analogue for the accumulated effect of oxidation over extended periods of time in soil. Biochar samples produced under subtly different conditions 122

- 123 can be readily distinguished and the oxidation treatment tuned to mimic the loss of C
- 124 occurring in charcoal over 50–200 yrs. in the environment (depending on ambient climate

125 conditions). The approach has potential to capture the effects of physical inaccessibility of126 biochar as a substrate, whereas thermal degradation may not.

A comprehensive comparison of the methods described is required for two reasons.
Firstly, if methods are equivalent or can be correlated, the more practical and cost effective
method may be promoted for future applications. Secondly, if results provided by different
methods diverge, new insights into the nature of biochar may emerge, for example, the effect
of contrasting abiotic conditions in the natural environment.

In the present study, a systematic set of biochar products was created from three contrasting feedstock materials using a single set of highly controlled small-scale pyrolysis equipment and defined temperature settings. The products were assessed using proximate analysis, elemental molar ratios and direct oxidation. The objective was to determine whether the different assessment methods provided a measure of the same characteristics and, where results showed different patterns, to consider the possible reasons.

138 Materials and Methods

139 *Feedstock*

140	The three types of biomass used in the pyrolysis experiments were: Pinus spp (mixed
141	pine wood chips, PC), Oryza sativa (rice husk variety, RH) and Triticum spp (wheat straw,
142	WS). Wood chips (ranging from $15 \times 5 \times 4$ mm to $100 \times 40 \times 15$ mm in dimension) were
143	acquired from Stonelaws Farm in East Lothian, Scotland. Rice Husk (uniformly less than 5 \times
144	4×1 mm particle size) was obtained from Kameoka, Kyoto Prefecture, Japan. Wheat straw
145	(primary fragments $10 \times 3 \times 1$ mm to $90 \times 5 \times 4$ mm) was purchased from StrawPellet Ltd.,
146	Rookery Farm, Lincolnshire, England. For pine wood chips and wheat straw the natural
147	heterogeneity within bulk supply was minimised as far as possible by thoroughly mixing a
148	volume sufficient for all experiments. The moisture content of each feedstock was
149	determined gravimetrically by drying at 105°C for 24 hr. Results from ultimate and proximate
150	analysis of the selected materials are shown in Table 1.

151

Table 1: Ultimate and proximate analysis for pine, rice husk and wheat straw feedstock usedin experimental work.

Feedstock	Fixed C %	Volatile Matter %	Ash %	Moisture %	C%	H%	N%	S%	O%*
Pine	21.6	73.2	2.0	3.3	49.5	5.9	0	NM	44.7
Rice Husk	15.0	59.4	21.3	4.3	37.9	4.9	0	NM	57.2
Wheat Straw	14.4	75.3	6.3	4.1	41.4	5.6	0	NM	53.1

154 NM, not measured

155 *, determined by difference

157 Equipment

Pyrolysis was conducted using the apparatus shown in Fig. 1 comprising a static bed reactor formed from a vertical 50 mm diameter quartz tube with sintered plate at the base allowing a sample bed depth of approx. 200 mm.



Fig. 1: Schematic of small scale laboratory batch pyrolysis unit situated at UKBRC, TheUniversity of Edinburgh.

164

161

The sample in the reactor tube was heated by a 12 kW infra-red gold image furnace 165 166 (P610C; ULVAC-RIKO, Yokohama, Japan) with a proportional-integral-derivative (PID) controller giving a wide range of heating rates and hold times with a maximum temperature 167 168 of 1300°C. Monitoring and control of temperature in the sample bed used a thermocouple positioned 10 mm from the inner surface of the quartz tube. Nitrogen gas (N₂) was supplied 169 to the bottom of the pyrolysis tube at a controlled rate. After preheating at the base of the 170 reactor, the gas passes up through the sample, sweeping volatiles and syngas into a 171 172 condensation system consisting of two sections. The first is heated $(160\pm10^{\circ}C)$; it removes entrained particulates on a filter and collects high-boiling tars in a separate trap. The second 173

section consists of a series of condensers and receivers where further condensable liquid
products are collected (Fig. 1). Data for the main process variables, temperature, pressure and
gas volume flow, are logged in real time.

177

178 Pyrolysis

179 Each pyrolysis experiment used a standard volume of feedstock, resulting in a different mass of material being used in runs for different feeds: 40g for pine chips, 30 g rice 180 husk or 15 g wheat straw. In a typical pyrolysis experiment biomass was charged into the 181 182 sample tube before the glassware system was assembled. The pressure sensors were zeroed and the system was purged with N₂ before establishing a steady N₂ flow rate of 0.33 L min⁻¹ 183 as carrier gas (giving a linear cold flow velocity within the empty pyrolysis tube of 184 approximately 3 mm s⁻¹). Samples from all feedstock types were heated at a rate of 5°C min⁻¹. 185 For pine chip and rice husk only 100°C min⁻¹ was also used for comparison. Hold 186 temperatures of 350°C, 450°C, 550°C and 650°C were used and maintained for 20 minutes 187 before gradual cooling (with continued N₂ flow) until below 100°C (about 1 hr.). 188

After pyrolysis, product masses were determined for char and condensed liquids by 189 190 weighing equipment before and after experiments. Product gas volume was measured using a volumetric flow meter (Ritter, TG5) and gas mass determined by calculation following 191 composition analysis using a mass spectrometer (Hiden, HPR-20 QIC). Yields of each 192 193 product (syngas, condensable and char) were calculated as a proportion of the mass of dry feed. Char product was removed from the pyrolysis tube and retained for analysis. Condensed 194 liquid products comprising heavy tar and lighter oil fractions were collected and stored in a 195 196 refrigerator. Gas products were disposed of by venting after composition analysis and volume measurement. 197

Char samples were analysed by proximate analysis, ultimate analysis and oxidation. 200 Prior to analysis all samples were milled to a homogenous fine powder using a ball mill 201 (MM200; Retsch, Castleford, UK) and dried overnight at 105°C as standard practice prior to 202 203 shipment of samples for analysis. Proximate analysis of all biochar samples and 204 corresponding feedstock was carried out using thermal gravimetric analysis (TGA/DSC 1; Mettler-Toledo, Leicester, UK). Due to the small amount (mg) needed for TGA analysis 205 moisture can be rapidly absorbed by the sample during transport and handling prior to 206 analysis. Samples were first heated for 10 min at 105°C under N₂ to determine moisture 207 content; the temperature was then raised at 25°C min⁻¹ to 900°C where it remained for a 208 further 10 min to eliminate volatile matter. With air introduced to the system the sample is 209 finally combusted (also at 900°C) for 15 minutes in order to determine ash. Fixed C is 210 211 calculated on a weight per cent basis by subtracting moisture, volatile and ash values from the original mass. Elemental (ultimate) analysis of C, H and N was conducted in duplicate using 212 an elemental analyser (Flash 2000, CE Elantech Inc, New Jersey, USA) by London 213 Metropolitan University (London, UK). The O content was determined by difference. 214 The Edinburgh stability tool, used in this study, has been developed by A. Cross and 215 S.P. Sohi at the UK Biochar research Centre, Edinburgh (Cross & Sohi 2012). Direct 216 oxidation was conducted at the University of Edinburgh by A. Cross and K. Crombie. This 217 stability assay forms part of a set of laboratory methods intended to provide a comprehensive 218 219 set of functional assays for biochar. Briefly, biochar containing 0.1 g C is milled to a fine powder to remove any potential effect of physical structure and is treated in a test tube with 7 220 ml of 5% H₂O₂, initially at room temperature and then at 80°C for 48 hr. during which time 221 222 the reaction is completed and the sample dried. Stable C is expressed as the percentage of the

initial 0.1g C that remains after oxidation, assessed from the gravimetric mass loss and
determinations of C content before and after oxidation (Cross & Sohi 2012)

225

226 Statistical Analysis

Correlations between analytical measures of biochar stability as well as analysis of 227 228 variance (ANOVA) were performed using Minitab 16 statistical software. The ANOVA statistical test was applied through a general linear model and significance of results were 229 calculated using Tukey's HSD (Honestly Significant Difference) at a significance level of P < 230 0.05 for all materials and production conditions. Labelling systems exist to attempt to 231 categorize R values by considering correlation coefficients < 0.35to represent low or weak 232 correlations, 0.36 to 0.67 to be moderate correlations, 0.68 to 1.00 strong or high correlations 233 and ≥ 0.9 to be a very high correlation (Taylor 1990). 234

Results and Discussion

Product Yield Distributions

- 237 The yields of char, liquid and gas obtained from each pyrolysis experiment are shown
- 238 in Fig. 2 a, b, c.



Fig. 2: Effect of production temperature on the product distribution yield for (a) char (b)liquids (c) gases present on a dry feed weight basis.

For each feedstock, higher pyrolysis temperatures resulted in a lower char yield, as 243 expected (Antal & Grønli 2003). The distribution of product char, liquid and gas was heavily 244 dependent on the original composition of biomass prior to pyrolysis. The cellulose, 245 hemicellulose and lignin fractions can vary greatly between feedstock materials and these 246 differences potentially result in contrasting product yields from pyrolysis and also the 247 properties of those products (Vassilev et al. 2010). The lower biochar yields given at higher 248 temperatures are a result of greater decomposition of organic material at higher temperatures 249 promoting the release of volatile material. Differences in volatile material yields over the 250 251 temperature range can be a result of the degree of breakdown of cellulose, hemicellulose and lignin (Demirbas 1994, 2002; Mohan et al. 2006; Enders et al. 2012). Rice husk samples 252 yielded the largest mass of char, but conserved mass included high concentrations of 253 254 inorganics present in the feedstock known from literature to be high in silica (Kalapathy et al. 2000). Increased char devolatilisation at higher temperature then results in a higher 255 percentage of liquid and gaseous products (Fig. 2b,c). The differences in yields with 256 257 production conditions could have an impact on the energy distribution between the char, liquid and gas products. In addition to biochar properties the distribution of the pyrolysis 258 products should be considered when selecting production conditions, since their quality and 259 quantity will determine their end use and so the overall impact of the system (Shackley et al. 260 2011). 261

262 *Direct Oxidation (Edinburgh stability tool)*

263 Stable C (biochar wt%), determined by the direct oxidation method (Cross & Sohi
264 2012), increased with pyrolysis temperature, for each feedstock (Fig. 3a).

265



266

Fig. 3: Effect of increasing production temperature on the (a) Stable C and (b) Stable C yield
of biochar samples. Error bars were added to the graph to show standard error of Stable C%
but are not visible due to the scale of the data (n=3)

270

Biochar produced from wheat straw contained the highest concentration of stable C at temperatures < 650°C however analysis of wheat straw biochar produced > 650°C exhibited a decrease in stable C. The higher stable C concentration at 550°C could be attributed to the heterogeneous nature of the wheat straw used for that experimental run resulting in an increased proportion of stable C present in the feedstock. Expressing results on a feedstock weight basis removes the direct effect of (conserved) feedstock ash content, although ash may still have influenced the product yields and biochar stability indirectly during the pyrolysis process (Fig. 3b). This measure provides an index for the efficiency of conversion of
feedstock C to stable C, rather than simply how much of the C in a particular biochar is
stable.

In contrast to the yield of biochar from pyrolysis, there was only a minor effect on stable C yield created in the pyrolysis of pine chips or wheat straw in the $350-650^{\circ}$ C range of pyrolysis temperature. Despite this small variation for wheat (22.6 - 28.9 %) and pine (22.0 - 24.8 %) derived biochar, the stable C yield for rice husk samples increased from 21.6 - 40.6% points when pyrolysis occurred at temperatures above 450° C. This observation could be a result of the high ash content typical for rice husk.

Heating rate, across the wide range of 1 to 100°C min⁻¹ investigated, did not seem to 287 have a notable impact on the concentration of stable C in biochar although a trend showing 288 289 slightly lower stable C yields in samples created at high heating rate could be discerned (reflecting lower char yields at higher heating rate). Lower variation in the yield of stable C 290 with increasing pyrolysis temperature is of particular importance to the economic and 291 environmental case for biochar production. Establishing how pyrolysis-biochar systems can 292 be optimised for product that best enhances soil fertility and sequesters C, while also 293 294 providing energy capture has been a key question. If the yield of stable C remains largely unaffected with increasing temperatures then biochar production could be tuned to maximise 295 296 energy as well as other physiochemical properties while maintaining the C sequestration 297 potential. The utility of high temperature biochar for soil fertility must then be considered.

298 Proximate Analysis

Results of proximate analysis are presented in Table 2. The ash concentration of biochar samples were influenced mainly by feedstock (P < 0.0001) and to a lesser extent by pyrolysis temperature (P = 0.003) with ash content increasing with temperature from wheat

302 straw and rice husk biochar (up to 20% and 50% respectively) but not for biochar from pine (<5%). In contrast to ash, fixed C and volatile matter on a dry ash free basis depended greatly 303 on temperature (P < 0.0001) with no influence from feedstock (P = 0.11). When ash content 304 was taken into account, however, feedstock had a significant effect (P < 0.0001). A strong 305 negative correlation between ash and fixed C ($R^2 = -0.808$, P < 0.0001) can be used to reflect 306 why all biochar samples produced from low ash pine contained high levels of fixed C 307 whereas high ash rice husk biochar exhibited low volatiles and fixed C concentrations. The 308 effect of ash on fixed C content produces a possible limitation of using proximate analysis for 309 310 the determination of a stable fraction. This is due to the decreasing measured weight of ash leading to inflated values for fixed C determined via subtraction. The loss in weight 311 associated with ash content can be due to volatilisation of ash species such as phosphorous 312 313 and magnesium during thermal treatment leading to problems of fouling, corrosion and slagging and. (Ali et al. 1988; Darvell et al. 2005, Sonoyama et al. 2006). 314

The fixed C content of biochar increased with pyrolysis temperature due to increasing concentrations of volatile matter being released. Samples produced from pine feedstock showed the highest concentration of volatile matter, as well as the largest decrease (from 55.4% to 14.8%) as temperature increased from 350 to 650°C.

Expressed on a feedstock basis the yield of fixed C increased up to 450°C but not at
higher temperatures (Fig. 4a).



321

Fig. 4: Influence of temperature on the (a) fixed C yield and (b) volatile matter yield ofbiochar samples produced from pine, rice husk and wheat straw

324

This confirmed the observations of others (Antal & Gronil 2003; Mašek *et al.* 2011) and suggested that certain functional properties enhanced at higher temperature could be acquired without diminishing C sequestration. As volatile matter follows the reverse pattern to fixed C (Fig. 4b), higher temperature pyrolysis might minimise the biochar fraction susceptible to decay in soil while increasing by-products for heat and energy generation. Since small fractions of volatile matter could prove either beneficial (Elad *et al.* 2010; Graber 331 et al. 2010) or detrimental (Jones et al. 2011) to different microbial communities in soil, the composition and ideal amount of volatile matter might need to be researched and quantified. 332 During proximate analysis the biochar sample is exposed to high analytical temperatures 333 which when compared to environment soil conditions can be considered to be extreme 334 therefore minimising the determined stability of carbon. Despite the term, "fixed C" is 335 336 calculated by weight difference rather than quantification of elemental C and will contain other species of high thermal stability. This combined with the release of volatiles and alkali 337 metals (P, K, As, Se, Hg etc) from the ash phase can lead to an inaccurate determination of C 338 derived from proximate analysis that could be deemed environmentally stable. 339

		Proximate analy	sis *	
Sample	Fixed C %	Volatile Matter %	Ash %	Total %
Pine 350-5	47.8	50.8	1.4	100
Pine 450-5	62.2	34.9	2.9	100
Pine 550-5	73.9	22.0	4.2	100.1
Pine 650-5	78.9	15.2	5.9	100
Pine 350-100	58.0	38.7	3.4	100.1
Pine 450-100	63.6	33.0	3.4	100
Pine 550-100	77.7	21.6	0.7	100
Pine 650-100	81.6	13.4	5.0	100
RH 350-5	32.4	30.3	37.3	100
RH 450-5	36.4	19.1	44.5	100
RH 550-5	38.5	14.6	46.9	100
RH 650-5	40.5	9.3	50.3	100.1
RH 350-100	39.3	20.7	40.1	100.1
RH 450-100	35.0	19.4	45.6	100
RH 550-100	37.0	11.3	51.7	100
RH 650-100	38.6	11.3	50.0	99.9
WS 350-5	49.5	39.6	10.9	100
WS 450-5	59.2	23.2	17.6	100
WS 550-5	62.8	17.2	20.0	100
WS 650-5	64.4	14.2	21.3	99.9

Table 2: Proximate analysis data for biochar samples produced from selected feedstock at

four temperatures (350, 450, 550 and 650° C) and two heating rates (5 and 100° C min⁻¹)

342 *, Moisture free basis

343 Ultimate Analysis

Results for all biochar samples are shown in Table 3. Statistical analysis indicated that temperature (P < 0.0001) was the main determinant of CHNO results expressed on a dry ash free basis. However, similar to proximate analysis, when the ash concentration was not included in the CHNO results, the impact of feedstock increased (P = 0.547, P = 0.001) to 348 becoming equally important as pyrolysis temperature. For biochar from each feedstock, biochar C content increased with pyrolysis temperature (and inversely to biochar yield) 349 through preferential elimination of N, H and O in volatile matter. Loss of O and H can be 350 351 attributed to the scission of weaker bonds within the char structure such as alky-aryl ether bonds and the formation of more resistant structures (Demirbas 2004). Total C content for all 352 biochar samples were considerably greater than the total C of their respective biomass. 353 However, when biochar yield was taken into account and total C expressed on a feedstock 354 weight basis it was found (Fig. S1) to be largely independent of pyrolysis temperature (as 355 356 with fixed and stable C yields).

The effect of elemental composition on the molar ratios O:C and H:C was assessed 357 (Fig. S2). All biochar samples had lower H:C and O:C ratio than their parent biomass owing 358 to preferential elimination of O and H relative to C in volatile matter. Due to the use of molar 359 ratios, small changes in H content had a proportionally larger effect on H:C than the 360 respective changes in O. Both ratios decreased in biochar with increasing pyrolysis 361 temperature. The ratio of H:C at each temperature decreased in the order WS > RH > P, 362 363 implying that pine feedstock yielded biochar of the highest stability – a alternative outcome to that obtained from O:C and stable C analysis. 364

Van Krevelen diagrams plot H:C against O:C to provide clear, visual indication for the origin and maturity of petroleum and coal and more recently applied to biochar to demonstrate the evolution of composition with temperature (Hammes *et al.* 2006; Preston & Schmidt 2006). In Fig. 5, samples from the current work are identified by feedstock and grouped graphically by pyrolysis temperature.



Fig. 5: Van Krevelen diagram comparing the O:C and H:C ratios of biochar samples withguidelines obtained from literature.

Biochar samples residing furthest to the right on the O:C scale were produced at 374 350°C, with those created at higher temperature grouped progressively closer to the origin. 375 Results for additional materials in the literature have been added to Fig. 6, to indicate how the 376 present samples compare to coal and lignite (Hammes *et al.* 2006; Van der Stelt *et al.* 2011) 377 as well as the regions of stability defined by Spokas (2010) and classification guidelines for 378 biochar (IBI Guidelines 2012; Schmidt *et al.* 2012).

379

			τ	Jltimate analy	vsis †	
Sample	C%	H%	N%	O%*	O:C atomic ratio	H:C atomic ratio
Pine 350-5	69.64	3.79	0.00	26.58	0.29	0.65
Pine 450-5	79.86	2.68	0.00	17.47	0.16	0.40
Pine 550-5	89.93	1.57	0.00	8.50	0.07	0.21
Pine 650-5	94.61	1.97	0.00	3.42	0.03	0.25
Pine 350-100	70.97	4.94	1.37	22.73	0.24	0.83
Pine 450-100	77.34	3.72	1.01	17.93	0.17	0.57
Pine 550-100	82.32	2.96	0.84	13.88	0.13	0.43
Pine 650-100	87.89	2.35	1.47	8.29	0.07	0.32
RH 350-5	66.14	4.67	0.00	29.19	0.33	0.84
RH 450-5	74.93	4.11	0.00	20.97	0.21	0.65
RH 550-5	84.03	3.43	0.00	12.54	0.11	0.49
RH 650-5	95.13	2.85	0.00	2.02	0.02	0.36
RH 350-100	70.87	5.36	0.00	23.77	0.25	0.90
RH 450-100	76.86	4.26	0.00	18.88	0.18	0.66
RH 550-100	89.98	3.61	0.00	6.40	0.05	0.48
RH 650-100	89.61	2.74	0.00	7.64	0.06	0.36
WS 350-5	70.88	5.46	1.71	21.96	0.31	0.92
WS 450-5	83.11	5.40	1.36	10.12	0.12	0.77
WS 550-5	86.21	3.63	0.81	9.36	0.11	0.50
WS 650-5	94.90	3.68	1.53	0.00	0.00	0.46

Table 3: Ultimate analysis of C, H, N and O for all biochar samples and corresponding O:C

381 and H:C ratios

382 *, determined by difference

383 † Dry ash free basis

Individually, five approaches to comparing the stability of biochar suggested 386 increasing biochar stability with higher pyrolysis temperature: increases in stable C, fixed C 387 content and a decrease in volatile matter, O:C and H:C. To assess relationships between the 388 different analytical techniques for stability, the results were plotted against each other in 389 correlation diagrams and presented in Fig. 6 with accompanying correlation coefficient R 390 values. As stable C determined by the Edinburgh stability tool is calculated on a dry ash free 391 basis the results for fixed C, volatile matter and elemental ratios were also converted to a dry 392 393 ash free basis to minimise variability of ash content between feedstock types. Heating rate was found to have no statistical effect (P > 0.5) on fixed C, volatile matter, stable C and O:C 394 ratio however significant effect was observed for feedstock on H:C ratio (P = 0.007). 395

396 The results from direct oxidation were correlated with H:C and O:C for each individual feedstock as well as a total correlation of all the data. In most cases the 397 correlations were considered to be very strong for all feedstock at both heating rates. Strong 398 correlation between stability indicators for samples produced for the same feedstock does not 399 confirm compatibility between methods for more diverse samples from multiple types of 400 401 biomass. The differing gradient of correlation coefficients between the feedstock and therefore overall scatter of data points should also be considered when reviewing the 402 403 compatibility between analytical methods for determining stability.

404



406 Fig. 6: Comparison of results between the Edinburgh stability data and alternative methods
407 for biochar stability: proximate and elemental analysis, (a) Stable C vs O:C ratio (b) Stable C
408 vs H:C ratio (c) Stable C vs fixed C (d) Stable C vs volatile matter

409	When comparing the correlation of stable C vs O:C/H:C for all samples (Fig. 6a,b),
410	increased scatter of the H:C values resulted in lower correlation coefficients ($R = -0.645$, $P =$
411	0.002) compared to that for O:C (R = -0.847, P < 0.0001). This large scatter could be due to
412	the trend previously mentioned (Fig. S2b), where at any of the selected production conditions
413	the H:C ratio follows a decreasing trend of $WS > RH > P$. This observed trend indicates that
414	the variation in H:C ratio could be influenced to a greater extent by feedstock properties
415	compared to that of O:C, confirmed by the higher statistical dependency of H:C ($P < 0.0001$)
416	than O:C ($P = 0.064$). The strong influence of feedstock on H:C ratio is derived from the
417	enhanced impact of feedstock on H concentration ($P < 0.0001$, dry ash free basis) whereas O
418	content is not influenced by feedstock ($P = 0.075$). As seen in Table 3 biochar samples
419	produced from pine and rice husk under the same production conditions contain similar
420	concentrations of C which also applies to wheat straw biochar produced at higher
421	temperatures (\geq 550°C). The decreasing trend (WS > RH > P) of H content present in the
422	biochar samples therefore resulted in higher H:C ratios. The absent effect of feedstock on O
423	content could stem from its determination based on subtraction rather than analytical
424	measurement of the O concentration. This approach can lead to inaccuracy in the
425	quantification of O due to assumptions made over the composition of biochar. Therefore O
426	derived data can influence the correlation with other measures of stability while failing to
427	demonstrate the significance of external factors such as feedstock.

Strong correlation was observed when comparing direct oxidation with fixed C (Fig. 6c) or volatile matter (Fig. 6d) for each feedstock and heating rates (R = 0.793, P < 0.0001). Identical R values were observed for both graphs demonstrating the relationship between decreasing volatile matter and the resulting increase in fixed C concentration. The overall spread of data within both graphs is potentially due to the influence of the varying ash concentration of high (RH), medium (WS) and low (P) present in the char samples as well as

any impact of heterogeneous feedstock samples. The correlation between the varying
methods could be influenced by the volatilisation of ash components during proximate
analysis.

Correlations between the more established analytical methods for stability indication 437 of fixed C vs O:C, fixed C vs H:C, volatile matter vs O:C and volatile matter vs H:C were 438 carried out and shown in Fig. S3. Strong correlations were again demonstrated for each 439 feedstock at both heating rates as well as the total correlation of the whole data set (R > 0.93). 440 Overall correlation values were representative of weaker correlation when comparing 441 proximate data against H:C (R = -0.806, P < 0.0001) rather than against O:C (R = -0.888, P <442 0.0001) however both correlations were determined to be strong. Increased scatter can be 443 seen in graphs comparing fixed C/volatile matter with H:C ratio, similar to that shown in Fig. 444 6b, although not to as great an extent, demonstrating the larger spread in H:C for all biochar 445 samples reiterating the impact of feedstock on H:C determination and therefore it's 446 correlation with proximate analysis data. 447

Samples for which divergence is observed between methods or where the scatter in
the relationship is enhanced can provide clues for revealing the strength, mode and
susceptibilities of each method to external influences and therefore evaluate the comparison
to soil conditions when biochar will ultimately degrade.

453 Conclusion

454 A new method of direct chemical oxidation of biochar, alongside three candidate methods for determination of relative biochar stability, i.e. fixed carbon content, O:C and 455 456 H:C ratios, was applied to a systematic set of biochar samples to indicate their relative stability. The results showed that temperature had the strongest effect on stability of biochar, 457 with stability increasing with maximum treatment temperature (at constant residence time at 458 peak temperature). However the yield of stable C, fixed C and total C were found to be 459 independent of temperature for biochar prepared from low ash feedstock (pine and wheat 460 461 straw). On the other hand the stable C yield of biochar produced from high ash biomass (rice husk) was seen to increase above 450°C creating two levels for stable C yield between 350-462 450°C and 550-650°C. Therefore increasing pyrolysis temperature could be utilised to 463 optimise additional benefits such as structural, chemical and energy generation without 464 sacrificing the C sequestration potential. 465

Comparison of results from direct oxidation of biochar with stability indicators 466 derived from proximate and ultimate analysis showed a strong correlation between the 467 approaches across feedstock and production conditions (pyrolysis temperature and heating 468 rate). However, despite the strong correlations, there was a sufficient degree of scatter, as 469 470 well as indication of different sensitivities to feedstock properties, that would reduce practical 471 usability of these correlations for predictive purposes. The results of this paper aim to 472 highlight the sensitivity of the current methods for stability assessment while proving valuable in defining protocols for defining stability or developing new improved methods. 473

The analysis of a systematic set of biochar samples generated using a small scale batch pyrolysis unit capable of accurately replicating production conditions allowed for the detailed investigation of varying biochar properties with experimental conditions. However the reproducibility of these results and therefore technique correlation could quite possibly

vary greatly depending on pyrolysis unit as well as scale of production. Therefore the
collection and analysis of samples from various pyrolysis units on differing scales using a
variety of production conditions would utilise a wider range of variables which can then be
statistically analysed for significance to biochar properties and used as calibration to improve
the prediction of biochar stability in soil.



483 Acknowledgments

This research was supported by a Science and Innovation award from the Engineering
and Physical Sciences Research Council in the UK (EP/F017944/1) and laboratory and
pyrolysis infrastructure by grants from the Scottish Funding Council and the College of
Science and Engineering, University of Edinburgh. Dr Clare Peters, University of Edinburgh,
provided training in the use of laboratory assays.

489	References
490	Ali MW, Zoltai SC, Radford FG (1988) A comparison of dry and wet ashing methods for the
491	elemental analysis of peat. Canadian Journal of Soil Science xx: xxx-xxx
492	
493	Antal MJ, Grønli M (2003) The Art, Science and Technology of Charcoal Production.
494	Industrial and Engineering Chemistry Research, 42, 1619-1640
495	
496	ASTM Standard – D 1792 (1990) Standard method for Chemical analysis of wood charcoal.
497	
498	Baldock JA, Smernik RJ (2002) Chemical composition and bioavailability of thermally
499	altered Pinus resinosa (Red pine) wood. Organic Geochemistry 33, 1093-1109
500	
501	Cheng C, Lehmann J, Thies JE, Burton SD, Engelhard, MH (2006) Oxidation of black carbon
502	by biotic and abiotic processes. Organic Geochemistry 37, 1477-1488
503	
504	Cross A, Sohi S (2012) A method for screening the relative long-term stability of biochar.
505	Global Change Biology and Bioenergy: Biochar Special issue, in Press
506	
507	Darvell LI, Hrycko P, Jones JM, Nowakowski DJ, Pourkashanian M, Williams A (2005)
508	Impact of minerals and alkali metals on willow combustion properties. World Renewable
509	Energy Congress
510	

511	Demirbas A (2004) Effects of temperature and particle size on bio-char yield from pyrolysis
512	of agricultural residues. Journal of Analytical and Applied Pyrolysis, 72, 243-248
513	
514	Downie A, Crosky A, Munroe P (2009) Chapter 2: Physical properties of biochar. Biochar
515	for Environmental Management: Science and technology. Earthscan, London
516	
517	Enders A, Hanley K, Whitman T, Joseph S, Lehmann, J (2012) Characterization of biochars
518	to evaluate recalcitrance and agronomic performance. Bioresource Technology, 114, 644-653
519	Elad Y, David DR, Harel YM et al (2010) Induction of Systemic Resistance in Plants by
520	Biochar, a Soil-Applied Carbon Sequestering Agent. Disease Control and Pest Management
521	100
522	
523	Graber ER, Harel YM, Kolton M et al (2010) Biochar impact on development and
524	productivity of pepper and tomato grown in fertigated soilless media. Plant Soil 337, 481-496
525	
526	Hammes K, Smernik RJ, Skjemstad JO, Herzog A, Vogt UF, Schmidt MWI (2006) Synthesis
527	and characterisation of laboratory-charred grass straw (Oryza sativa) and chestnut wood
528	(Castanea sativa) as reference materials for black carbon quantification. Organic
529	Geochemistry 37 , 1629-1633
530	
531	Hedges JI, Eglinton G, Hatcher PG et al. (2000) The molecularly-uncharacterized component
532	of non-living organic matter in natural environments. Organic Geochemistry 31, 945-958
533	

534 International Biochar Initiative (IBI) Guidelines (2012) Standardized product definition and

535 product testing guidelines for biochar that is used in soil

536

- 537 Jones DL, Murphy DV, Khalid M, Ahmad W, Edward-Jones G, DeLuca TH (2011) Short-
- term biochar-induced increase in soil CO₂ release is both biotically and abiotically mediated.
- 539 Soil Biology and Biochemistry 43,1723-1731

540

- 541 Kalapathy U, Proctor A, Shultz J (2000) A simple method for production of pure silica from
- rice hull ash. *Bioresource Technology* **73**, 257-262
- 543 Kuhlbusch TAJ (1995) Method for determining black carbon in residues of vegetation fires.
- 544 Environmental Science and Technology **29**, 2695-2702

545

Kuhlbusch TAJ, Crutzen PJ (1995) Toward a global estimate of black carbon in residues of
vegetation fires representing a sink of atmospheric CO₂ and source of O₂. *Global Biogeochemical Cycles* 9, 491-501

549

Lehmann J, Czimczik C, Laird D, Sohi S (2009) Chapter 11: Stability of Biochar in Soil. *Biochar for Environmental Management: Science and technology*. Earthscan, London

552

Liang B, Lehmann J, Solomon D et al. (2008) Stability of biomass-derived black carbon in
soils. *Geochimica et Cosmochimica Acta* 72, 6069-6078

556 Mašek O, Brownsort P, Cross A, Sohi S (2011) Influence of production conditions on the 557 yield and environmental stability of biochar. *Fuel xxx-xxx*

558

559 Masiello CA (2004) New directions in black carbon organic geochemistry. *Marine*560 *Chemistry*, 92, 201-213

561

Mohan D, Pittman CUJr, Steele PH (2006) Pyrolysis of Wood/Biomass for Bio-oil: A
Critical Review. *Energy and Fuels*, 20, 848-889

564

Preston CM, Schmidt MWI (2006) Black (pyrogenic) carbon: a synthesis of current
knowledge and uncertainties with special consideration of boreal regions. *Biogeosciences*, 3,
397-420

568

Schmidt HP, Abiven S, Kammann C, Glaser B, Bucheli T, Leifeld J (2012) European
Biochar Certificate: Guidelines for biochar production

571

572 Shackley S, Sohi S, Brownsort P et al. (2009) An Assessment of the Benefits and Issues 573 associated with the Application of Biochar to Soil. *A report commissioned by the UK* 574 *Department for Environment, Food and Rural Affairs, and Department of Energy and* 575 *Climate Change*

576

577 Shackley S, Hammond J, Gaunt J and Ibarrola R (2011) The feasibility and cost of biochar

578 deployment in the UK. *Carbon Management*, **2(3)**, 335-356

579

- Spokas KA (2010) Review of the stability of biochar in soils: predictability of O:C molar
 ratios. *Carbon Management*, 1, 289-303
- 582
- 583 Sohi SP, Krull E, Lopez-Capel E, Bol R (2010) A Review of Biochar and its Use and
- 584 Function in Soil. *Advances in Agronomy* **105**, 47-82

585

586	Sonoyama N, Okuno T, Mašek O, Hosokai S, Li CZ, Hayashi J (2006) Interparticle
587	desorption and re-adsorption of alkali and alkaline earth metallic species within a bed of
588	pyrolyzing char from pulverized woody biomass. Energy & Fuels, 20, 1294-1297Taylor R
589	(1990) Interpretation of the Correlation Coefficient: A Basic Review. The Journal of Defence
590	Modelling and Simulation 1, 35-39
591	

- Van der Stelt MJC, Gerhauser H, Kiel JHA, Ptasinki KJ (2011) Biomass upgrading by
 torrefaction for the production of biofuels: A review. *Biomass and Bioenergy*, **35**, 3748-3762
- Vassilev SV, Baxter D, Andersen LK, Vassileva CG, Morgan TJ (2010) An overview of the
 chemical composition of biomass. *Fuel*, 89, 913 933

598 Supplementary Material

599 Carbon Yield results

As temperature is increased the concentration of C in biochar also increases. However, this is not the case for char yield is taken into consideration. By representing the total C on a feedstock weight basis there is little variation over the temperature range 350° C- 650° C as shown in Fig. S1.



Fig. S1: Variation of C yield with increasing production temperature. Error bars were added to the graph to show standard error of C% analysis but are not visible due to the scale of the data (n=2)



608

609 Fig. S2: Influence of temperature on the (a) O:C ratio and (b) H:C ratio of biochar samples

610 and parent biomass

612 *Correlation between Proximate and Elemental analysis*

The results obtain from proximate analysis were compared to those produced by elemental analysis to investigate the correlation between two different methods for stability determination. The correlation between techniques and accompanying R values are shown in Fig. S3





Fig. S3: Comparisons between proximate and elemental analysis data to show correlations
between (a) fixed C vs O:C ratio (b) fixed C vs H:C ratio (c) volatile matter vs O:C ratio (d)
volatile matter vs H:C ratio