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

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1 **THE EFFECT OF PYROLYSIS CONDITIONS ON BIOCHAR**
2 **STABILITY AS DETERMINED BY THREE METHODS**

3 Running Title - Crombie et al.: Assessing biochar stability

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17 **Keywords:** Biochar, carbon sequestration, pyrolysis, stability determination, Edinburgh

18 **toolkit, Stable carbon, physiochemical properties**

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24 **Primary Research Article**

25

26 **Abstract**

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

49

50

51 **Introduction**

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

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

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

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 D1762-
78 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).

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

88 Pyrolysis favours the elimination of H and O over C, such that extending pyrolysis
89 reactions results in a solid residue (char) of progressively higher C concentration. The utility
90 of elemental ratios, provided by ultimate analysis, as indicators of biochar stability has been
91 extensively researched (Kuhlbusch 1995; Hedges *et al.* 2000; Masiello 2004; Spokas 2010;
92 IBI Guidelines 2012; Schmidt *et al.* 2012). The O:C ratios assigned to materials encompassed
93 by the black C continuum showed a systematic increase from 0 for graphite to >0.6 for
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
100 biochar stability (Spokas 2010). This work proposed that biochar displaying an O:C ratio

101 >0.6 would be closer to biomass composition than to graphite and would have a mean
102 residence time <100 years. Conversely, material with an O:C ratio in the range 0.2–0.6 would
103 be expected to have mean residence time of 100–1000 years. To avoid confounding analyses
104 with non-black C species IBI guidelines for quantifying O:C ratio recommend the application
105 of an acid treatment for the removal of carbonates and determination of organic C (IBI
106 Guidelines 2012).

107 The ratio of H:C has also been proposed as an index of aromaticity and resistance of
108 char to microbial and chemical degradation (Kuhlbusch 1995; Kuhlbusch & Crutzen 1995).
109 As with O:C quantification, pre-treatment steps (acid and thermal treatment) can be applied
110 to remove inorganic and organic C prior to total H and C determination. Kuhlbusch (1995)
111 also described the use of a correction factor to exclude H bound to elements other than C,
112 most likely silicate and therefore generating an H:C ratio only for the stable fraction of char.
113 However, Enders *et al* (2012) showed that their results ranked poultry manure, based on H:C
114 ratio, to have equal stability to woody samples which were found to be much more stable thus
115 creating doubt over the suitability of H:C as a method of stability determination.

116 In order for the potential of biochar for C sequestration and agricultural benefit to be
117 fully realised, it is necessary that the different functional characteristics of biochar such as
118 stability can be rapidly assessed prior to deployment. The method put forward by Cross and
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 (H₂O₂) is used as an analogue for the accumulated effect of oxidation over
122 extended periods of time in soil. Biochar samples produced under subtly different conditions
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 of
126 biochar as a substrate, whereas thermal degradation may not.

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

132 In the present study, a systematic set of biochar products was created from three
133 contrasting feedstock materials using a single set of highly controlled small-scale pyrolysis
134 equipment and defined temperature settings. The products were assessed using proximate
135 analysis, elemental molar ratios and direct oxidation. The objective was to determine whether
136 the different assessment methods provided a measure of the same characteristics and, where
137 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 × 5 × 4 mm to 100 × 40 × 15 mm in dimension) were
143 acquired from Stonelaws Farm in East Lothian, Scotland. Rice Husk (uniformly less than 5 ×
144 4 × 1 mm particle size) was obtained from Kameoka, Kyoto Prefecture, Japan. Wheat straw
145 (primary fragments 10 × 3 × 1 mm to 90 × 5 × 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

152 Table 1: Ultimate and proximate analysis for pine, rice husk and wheat straw feedstock used
153 in 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

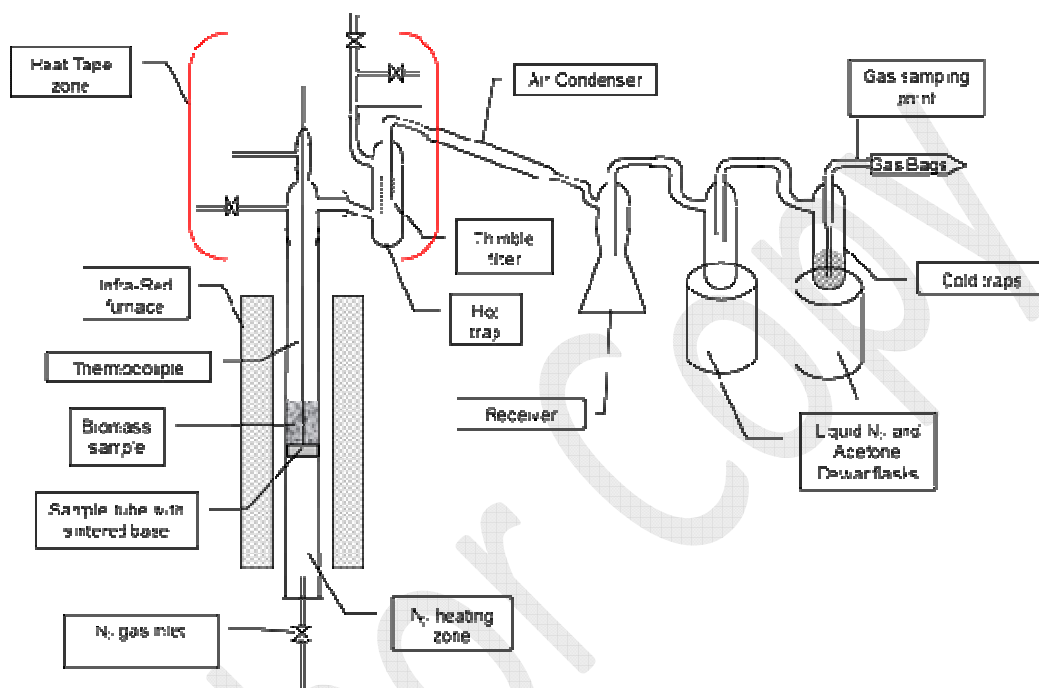
154 NM, not measured

155 *, determined by difference

156

157 *Equipment*

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



161
162 Fig. 1: Schematic of small scale laboratory batch pyrolysis unit situated at UKBRC, The
163 University of Edinburgh.

164
165 The sample in the reactor tube was heated by a 12 kW infra-red gold image furnace
166 (P610C; ULVAC-RIKO, Yokohama, Japan) with a proportional–integral–derivative (PID)
167 controller giving a wide range of heating rates and hold times with a maximum temperature
168 of 1300°C. Monitoring and control of temperature in the sample bed used a thermocouple
169 positioned 10 mm from the inner surface of the quartz tube. Nitrogen gas (N₂) was supplied
170 to the bottom of the pyrolysis tube at a controlled rate. After preheating at the base of the
171 reactor, the gas passes up through the sample, sweeping volatiles and syngas into a
172 condensation system consisting of two sections. The first is heated (160±10°C); it removes
173 entrained particulates on a filter and collects high-boiling tars in a separate trap. The second

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

177

178 *Pyrolysis*

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

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

198

199 *Analysis of biochar*

200 Char samples were analysed by proximate analysis, ultimate analysis and oxidation.
201 Prior to analysis all samples were milled to a homogenous fine powder using a ball mill
202 (MM200; Retsch, Castleford, UK) and dried overnight at 105°C as standard practice prior to
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;
205 Mettler-Toledo, Leicester, UK). Due to the small amount (mg) needed for TGA analysis
206 moisture can be rapidly absorbed by the sample during transport and handling prior to
207 analysis. Samples were first heated for 10 min at 105°C under N₂ to determine moisture
208 content; the temperature was then raised at 25°C min⁻¹ to 900°C where it remained for a
209 further 10 min to eliminate volatile matter. With air introduced to the system the sample is
210 finally combusted (also at 900°C) for 15 minutes in order to determine ash. Fixed C is
211 calculated on a weight per cent basis by subtracting moisture, volatile and ash values from the
212 original mass. Elemental (ultimate) analysis of C, H and N was conducted in duplicate using
213 an elemental analyser (Flash 2000, CE Elantech Inc, New Jersey, USA) by London
214 Metropolitan University (London, UK). The O content was determined by difference.

215 The Edinburgh stability tool, used in this study, has been developed by A. Cross and
216 S.P. Sohi at the UK Biochar research Centre, Edinburgh (Cross & Sohi 2012). Direct
217 oxidation was conducted at the University of Edinburgh by A. Cross and K. Crombie. This
218 stability assay forms part of a set of laboratory methods intended to provide a comprehensive
219 set of functional assays for biochar. Briefly, biochar containing 0.1 g C is milled to a fine
220 powder to remove any potential effect of physical structure and is treated in a test tube with 7
221 ml of 5% H₂O₂, initially at room temperature and then at 80°C for 48 hr. during which time
222 the reaction is completed and the sample dried. Stable C is expressed as the percentage of the

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

225

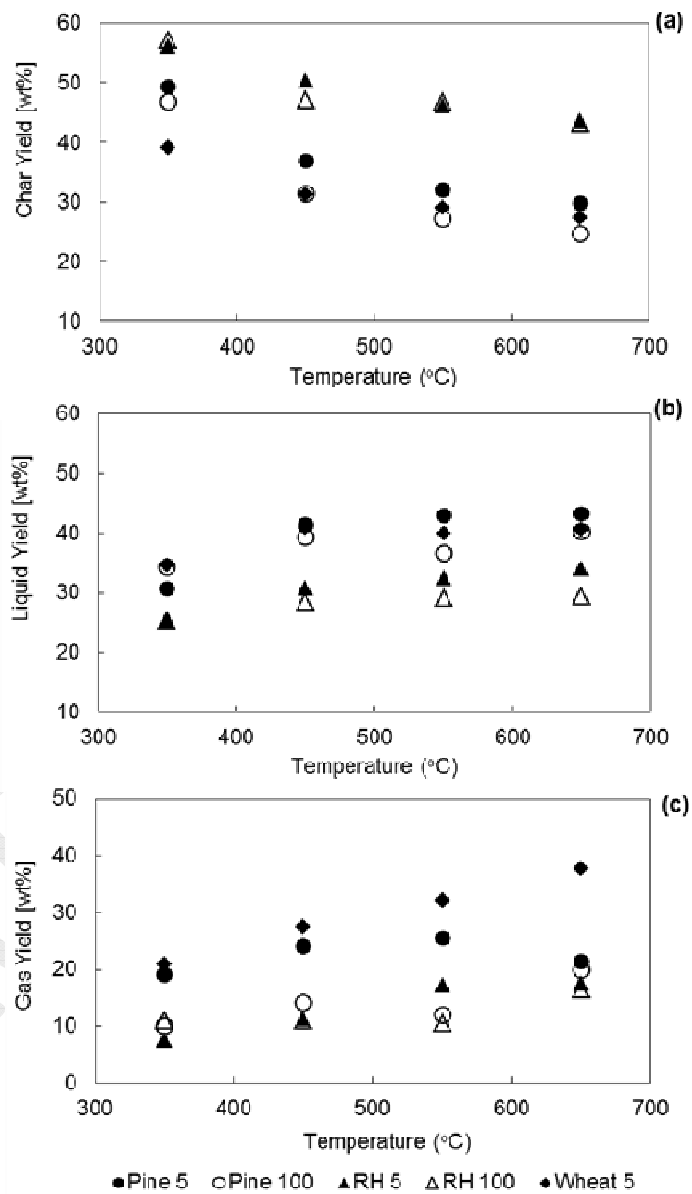
226 *Statistical Analysis*

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

235 **Results and Discussion**

236 *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.



239
240 Fig. 2: Effect of production temperature on the product distribution yield for (a) char (b)
241 liquids (c) gases present on a dry feed weight basis.

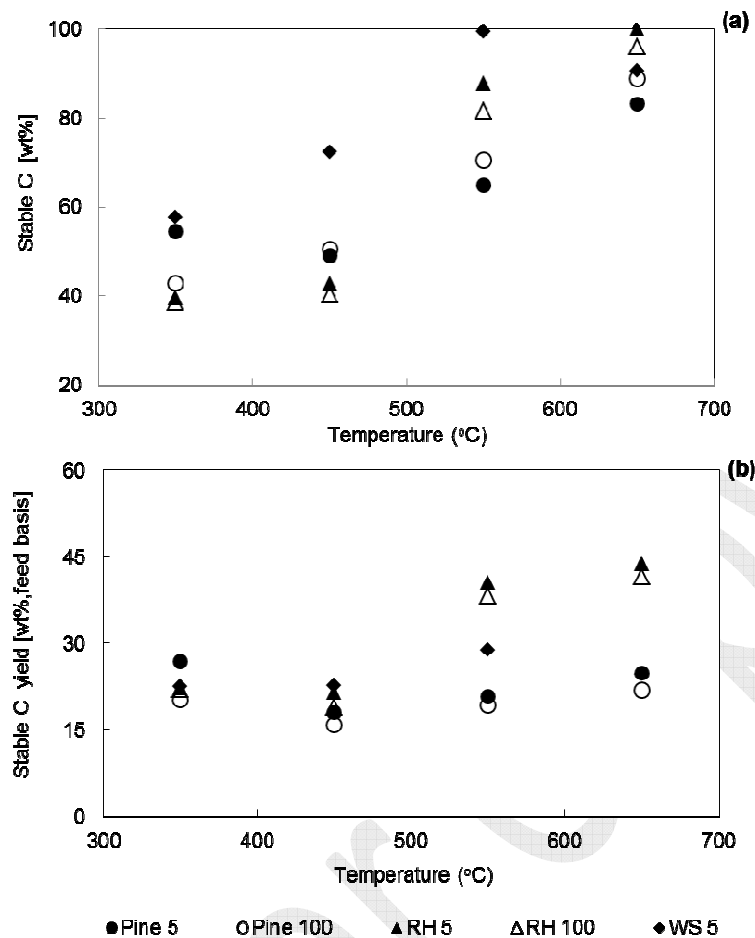
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243 For each feedstock, higher pyrolysis temperatures resulted in a lower char yield, as
244 expected (Antal & Grønli 2003). The distribution of product char, liquid and gas was heavily
245 dependent on the original composition of biomass prior to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

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

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

270

271 Biochar produced from wheat straw contained the highest concentration of stable C at
 272 temperatures < 650°C however analysis of wheat straw biochar produced > 650°C exhibited a
 273 decrease in stable C. The higher stable C concentration at 550°C could be attributed to the
 274 heterogeneous nature of the wheat straw used for that experimental run resulting in an
 275 increased proportion of stable C present in the feedstock. Expressing results on a feedstock
 276 weight basis removes the direct effect of (conserved) feedstock ash content, although ash may
 277 still have influenced the product yields and biochar stability indirectly during the pyrolysis

278 process (Fig. 3b). This measure provides an index for the efficiency of conversion of
279 feedstock C to stable C, rather than simply how much of the C in a particular biochar is
280 stable.

281 In contrast to the yield of biochar from pyrolysis, there was only a minor effect on
282 stable C yield created in the pyrolysis of pine chips or wheat straw in the 350–650°C range of
283 pyrolysis temperature. Despite this small variation for wheat (22.6 – 28.9 %) and pine (22.0 –
284 24.8 %) derived biochar, the stable C yield for rice husk samples increased from 21.6 – 40.6
285 % points when pyrolysis occurred at temperatures above 450°C. This observation could be a
286 result of the high ash content typical for rice husk.

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

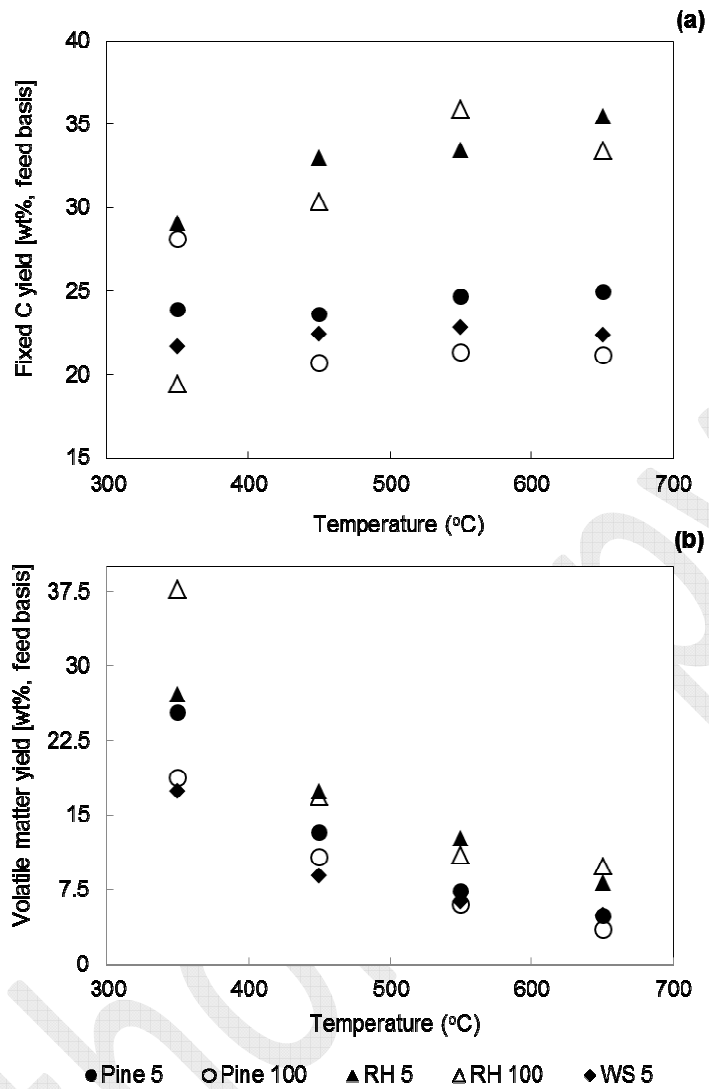
298 *Proximate Analysis*

299 Results of proximate analysis are presented in Table 2. The ash concentration of
300 biochar samples were influenced mainly by feedstock ($P < 0.0001$) and to a lesser extent by
301 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
303 (<5%). In contrast to ash, fixed C and volatile matter on a dry ash free basis depended greatly
304 on temperature ($P < 0.0001$) with no influence from feedstock ($P = 0.11$). When ash content
305 was taken into account, however, feedstock had a significant effect ($P < 0.0001$). A strong
306 negative correlation between ash and fixed C ($R^2 = -0.808$, $P < 0.0001$) can be used to reflect
307 why all biochar samples produced from low ash pine contained high levels of fixed C
308 whereas high ash rice husk biochar exhibited low volatiles and fixed C concentrations. The
309 effect of ash on fixed C content produces a possible limitation of using proximate analysis for
310 the determination of a stable fraction. This is due to the decreasing measured weight of ash
311 leading to inflated values for fixed C determined via subtraction. The loss in weight
312 associated with ash content can be due to volatilisation of ash species such as phosphorous
313 and magnesium during thermal treatment leading to problems of fouling, corrosion and
314 slagging and. (Ali *et al.* 1988; Darvell *et al.* 2005, Sonoyama *et al.* 2006).

315 The fixed C content of biochar increased with pyrolysis temperature due to increasing
316 concentrations of volatile matter being released. Samples produced from pine feedstock
317 showed the highest concentration of volatile matter, as well as the largest decrease (from
318 55.4% to 14.8%) as temperature increased from 350 to 650°C.

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



321

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

324

325 This confirmed the observations of others (Antal & Gronil 2003; Mašek *et al.* 2011)

326 and suggested that certain functional properties enhanced at higher temperature could be

327 acquired without diminishing C sequestration. As volatile matter follows the reverse pattern

328 to fixed C (Fig. 4b), higher temperature pyrolysis might minimise the biochar fraction

329 susceptible to decay in soil while increasing by-products for heat and energy generation.

330 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
332 composition and ideal amount of volatile matter might need to be researched and quantified.
333 During proximate analysis the biochar sample is exposed to high analytical temperatures
334 which when compared to environment soil conditions can be considered to be extreme
335 therefore minimising the determined stability of carbon. Despite the term, “fixed C” is
336 calculated by weight difference rather than quantification of elemental C and will contain
337 other species of high thermal stability. This combined with the release of volatiles and alkali
338 metals (P, K, As, Se, Hg etc) from the ash phase can lead to an inaccurate determination of C
339 derived from proximate analysis that could be deemed environmentally stable.

340 Table 2: Proximate analysis data for biochar samples produced from selected feedstock at
 341 four temperatures (350, 450, 550 and 650°C) and two heating rates (5 and 100°C min⁻¹)

Proximate analysis *				
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

342 *, Moisture free basis

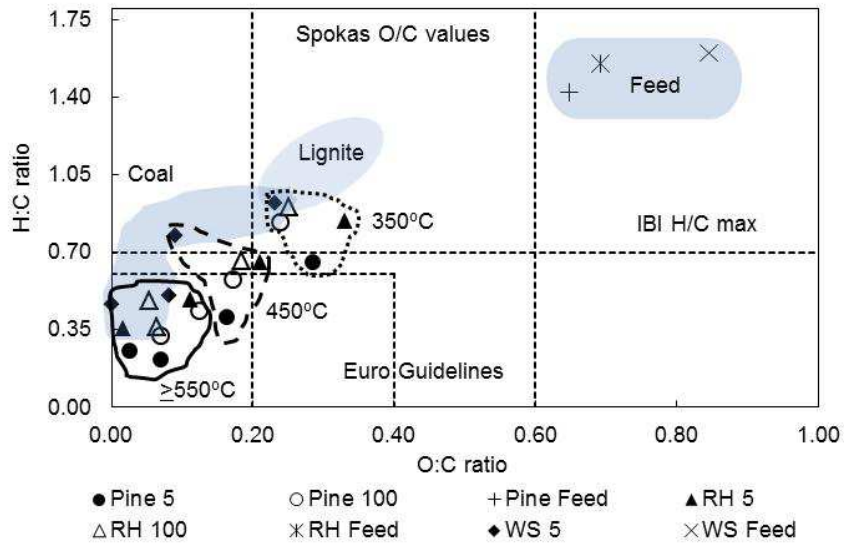
343 *Ultimate Analysis*

344 Results for all biochar samples are shown in Table 3. Statistical analysis indicated that
 345 temperature ($P < 0.0001$) was the main determinant of CHNO results expressed on a dry ash
 346 free basis. However, similar to proximate analysis, when the ash concentration was not
 347 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,
349 biochar C content increased with pyrolysis temperature (and inversely to biochar yield)
350 through preferential elimination of N, H and O in volatile matter. Loss of O and H can be
351 attributed to the scission of weaker bonds within the char structure such as alky–aryl ether
352 bonds and the formation of more resistant structures (Demirbas 2004). Total C content for all
353 biochar samples were considerably greater than the total C of their respective biomass.
354 However, when biochar yield was taken into account and total C expressed on a feedstock
355 weight basis it was found (Fig. S1) to be largely independent of pyrolysis temperature (as
356 with fixed and stable C yields).

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

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



370

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

373 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

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

Sample	Ultimate analysis †					
	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

382 *, determined by difference

383 † Dry ash free basis

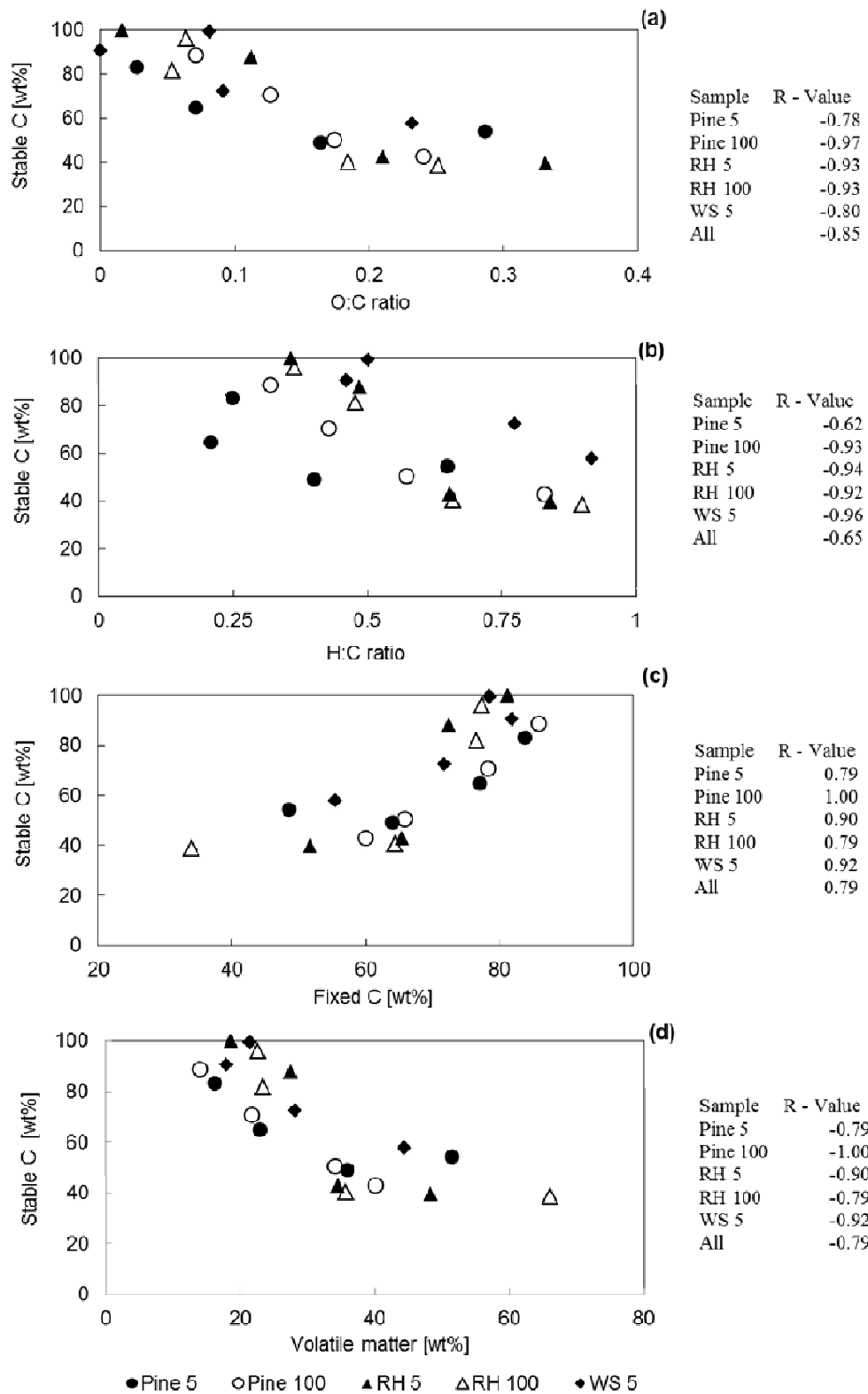
384

385 *Comparison of stability determination*

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

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

404



405

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 ($\geq 550^{\circ}\text{C}$). 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.

428 Strong correlation was observed when comparing direct oxidation with fixed C (Fig.
429 6c) or volatile matter (Fig. 6d) for each feedstock and heating rates ($R = 0.793$, $P < 0.0001$).
430 Identical R values were observed for both graphs demonstrating the relationship between
431 decreasing volatile matter and the resulting increase in fixed C concentration. The overall
432 spread of data within both graphs is potentially due to the influence of the varying ash
433 concentration of high (RH), medium (WS) and low (P) present in the char samples as well as

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

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

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

452

453 **Conclusion**

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

466 Comparison of results from direct oxidation of biochar with stability indicators
467 derived from proximate and ultimate analysis showed a strong correlation between the
468 approaches across feedstock and production conditions (pyrolysis temperature and heating
469 rate). However, despite the strong correlations, there was a sufficient degree of scatter, as
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
473 valuable in defining protocols for defining stability or developing new improved methods.

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

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

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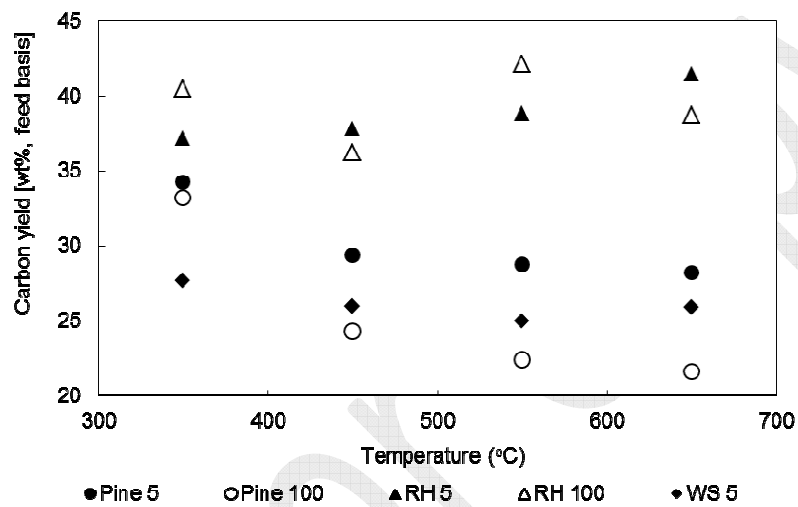
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598 **Supplementary Material**

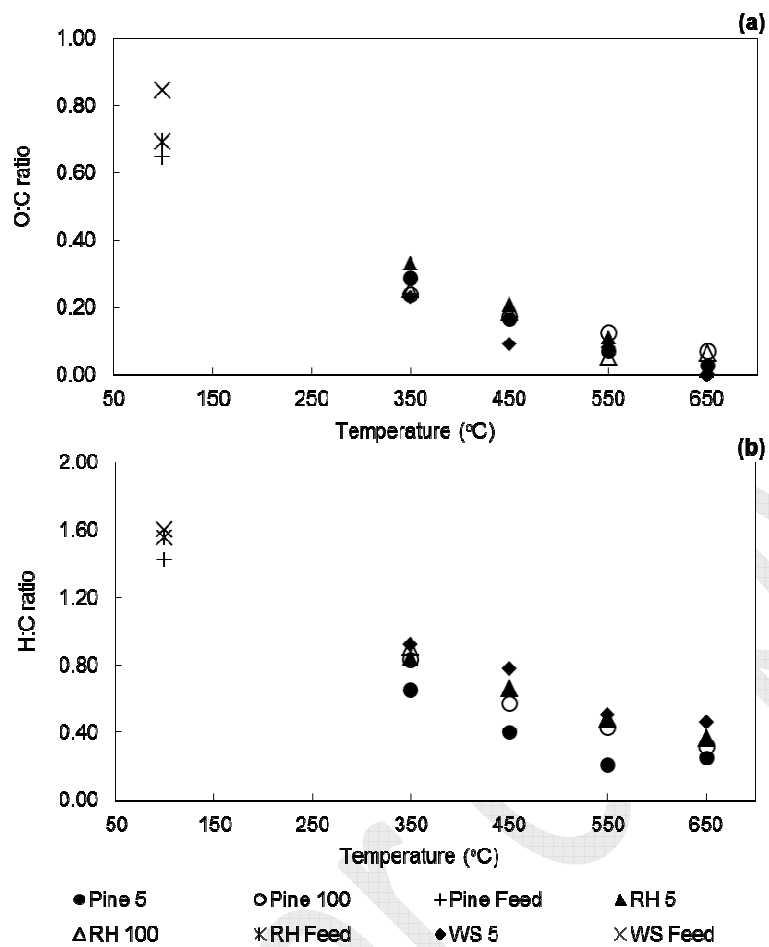
599 *Carbon Yield results*

600 As temperature is increased the concentration of C in biochar also increases.
601 However, this is not the case for char yield is taken into consideration. By representing the
602 total C on a feedstock weight basis there is little variation over the temperature range 350°C-
603 650°C as shown in Fig. S1.



604

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



608

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

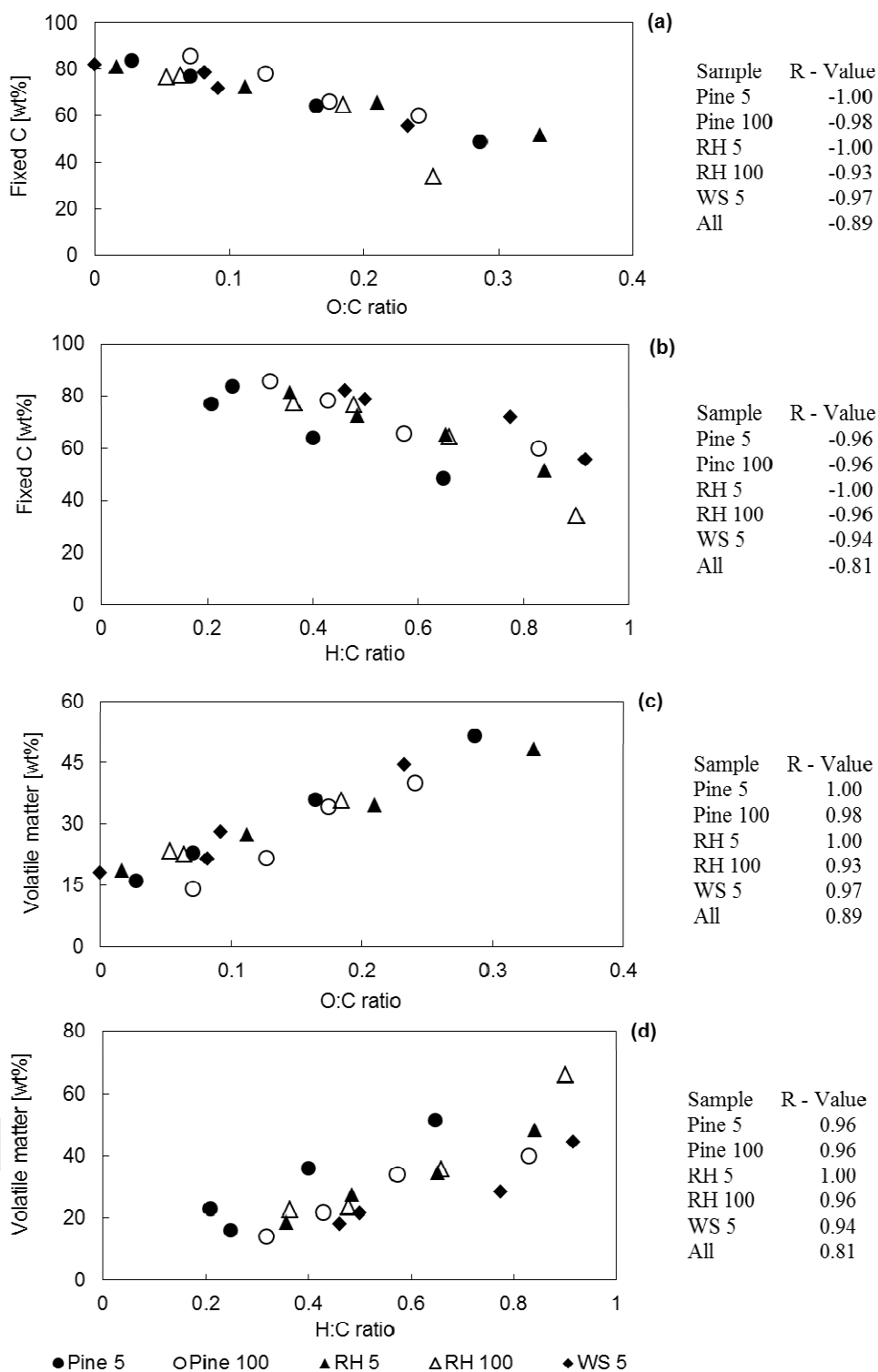
610 and parent biomass

611

612 *Correlation between Proximate and Elemental analysis*

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

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617

618 Fig. S3: Comparisons between proximate and elemental analysis data to show correlations

619 between (a) fixed C vs O:C ratio (b) fixed C vs H:C ratio (c) volatile matter vs O:C ratio (d)

620 volatile matter vs H:C ratio

621