

Dear Editor of Biogeosciences

Please find attached a revised version of the manuscript entitled, "*Physical and Chemical Characterization of Biochars Derived from Different Agricultural Residues*".

First of all, I would like to thank the referees whose suggestions have definitely improved the paper. All comments and corrections have been taken into consideration. Mainly, the sections of introduction and conclusion have been improved. Regarding improvement of English writing, we made a deep revision of the manuscript and, lately asked for professional editing services (Editage) to revise it.

Thank you very much,

Best regards,

KEIJI JINDO

Dear Referee #1,

Thank you very much for your suggestions, our response for your comments was described with blue colour as following:

Remarks from Referee#1

The ms. dealing with "Physical and chemical characterizations of biochars derived from different agricultural residues" is clear, well organised and written. For the future work, we suggest the authors to compare and discuss these results with those of standard of humic substances (humic acids, mainly) supplied by the IHSS (Internationa Humic Substance Society).

The comment of Referee #1 is relevant since there are similarities of chemical composition with humic subsatances, especially in terms of recalcitrant character. In fact, the technique to analysis of chemical composition of biochar material by FT-IR, NMR, and thermal analysis can be very fundamental tools to compare biochars to those materials.

Dear Referee#2

Thank you very much for your comments and suggestions, all of them have been considered in order to improve the quality of this paper. The comments of Referee#2 are relevant and reasonable. All our response for your comments was described with blue colour as following:

Remarks from Referee#2

In my opinion this article does not suit the aims and scope of biogeosciences. Different temperatures can alter the characteristics of biochar. But what is the implication that this has in the soil biogeochemistry or soil microbiology? This article is much more suited for a journal focused on pyrolysis like Journal of Analytical and Applied Pyrolysis. The article is not very well written, both with numerous grammar mistakes. See, for example, lines 11 and 21 in the abstract or the first line in the introduction. In many instances there are also inadequate links between ideas. The authors conclude that low temperature biochars are better for soil microbial population potential for carbon sequestration. There is not the level of novelty required to publish in Biogeosciences.

First of all, we appreciate your comments, which encouraged us to reconstruct the manuscript for making clearer the focus of our work and also to upgrade the manuscript quality.

We have now rewritten the aim of the manuscript (the last section of the introduction) to highlight the relevance of our work to the scope of the journal. The main aim was to optimize the physicochemical properties of biochar, prepared from different residual materials as feedstocks in order to enhance their potential as organic amendments and to interact with the different soil biogeochemical cycles. We hope that the new version clearly highlights the relationship of the paper to the following scope of the journal "Biogeochemistry and global elemental cycles".

In addition, we have included further characterization of the biochars in order to evaluate their stability in soils. The ash content of biochar and the thermal analysis are

added to our study. These data manifest the differences of the properties with more details.

Concerning of the use of English, we made a deep revision of the manuscript and ask for professional editing services (Editage) to revise our whole manuscript including tables and figures.

We have amended the sentence in the conclusions, and we have reviewed the entire manuscript to clarify well known concepts and the main contributions of this paper.

Page 11728, lines 1-6: This is mentioned only in the abstract and not in the introduction section. Lines 20-21: This is never proved in this article. These constitute examples of inadequate links between ideas.

We agree with the reviewer and we have focused the abstract on the novelty of the paper, rather than introducing the research topic.

Page 11729, line 10: This reference is a very poor choice here. Lammirato did not measure any indicator related to plant performance. Line 20: “Eucalyptus”

We appreciate the clarification and, accordingly, we have replaced the reference by Lammirato et al, 2011. We choose other references, relating to the experiment of plant growth (Robertson et al., 2012) and the nutrient release from biochar (Mukherjee and Zimmerman, 2013).

“Eucaryptus” was corrected to “Eucalyptus”.

There is a lack of hypothesis in the introduction. It is not clear what the authors aim to learn from this experiment. In addition they justify the use of rice husk and rice straw, but not other materials.

The revised version of the introduction was intended to better explain the aim of the paper. However, as suggested by the referee, we also included an statement with the hypothesis of the manuscript to justify how the different properties of the feedstock

would determine the behavior of biochar in soil and the impact on soil biogeochemical cycles. Justification of the use of apple pruning woodchip and the oak tree, as the reference as the hard-wood material was added.

Page 11730, line 8: What was the approximate size of the pieces? This has important implications for the pyrolysis process.

We agree with reviewer. The size of the pieces was less than 4–5 cm. The description was added in the manuscript.

Page 11732, lines 17-19: This is highly speculative. Lines 24 to end of the page: This is again highly speculative. How would Si content affect the pyrolysis process?

The sentence on the page 11732, lines 17-19, was omitted, and the sentence from Line 24 to end of the page was rephrased. A description of Si content during the pyrolysis process was added in the manuscript and supplementary data on elemental composition of biochars produced at 800 °C, including the Si content, is now shown.

Page 11733, lines 7-9: This sentence is really difficult to understand. It needs serious re-writing.

The sentence was rewritten.

Page 11736, line 1: As substitute for what?

It was error. It should be “substrate”.

1 **Physical and Chemical Characterizations of biochars derived from different**
2 **agricultural residues**

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Abstract

~~Biochar has received large attention as a strategy to tackle against carbon emission. Not only carbon fixation has been carried out but also other merits for agricultural application due to unique physical and chemical character such as absorption of contaminated compounds in soil, trapping ammonia and methane emission from compost, and enhancement of fertilizer quality. Biochar has been evaluated globally as a tool for carbon sequestration and soil fertility. The understanding of the chemical and physical properties of biochar, which are strongly related to type of original material and pyrolysis condition, is an important key to identifyselect the most suitable use in lately adequate application to soil (Manya, 2012).~~

A selection of organic wastes with contrasting characteristics (rice husk, rice straw, wood chips of apple tree (*Malus Pumila*) and oak tree (*Quercus serrata*)) were pyrolyzedpirolyzed at different temperatures (400, 500, 600, 700 and 800°C) in order to optimize the physicochemical properties of biochar as soil amendment. In order to evaluate and optimize those characteristics of the pyrolysis product, several chemical and physical analysis were examined in our studyIn our study, using different local waste feed stocks (rice husk, rice straw, wood chips of apple tree (*Malus Pumila*) and oak tree (*Quercus serrata*)), in Aomori, Japan, were utilized for creating biochar with different temperature (400,500,600,700,and 800°C). Concerning to the biochar production, theP pyrolysis of at lower temperatures produced high had more biochar yields, but , in relative to tha_n higher temperature pyrolysis process. On the contrary,produced biochars with high C content, surface areas and adsorption characteristics have been increased as increasing temperature. The proportions of

53 ~~carbon content in the biochars also increased together with increased temperatures.~~
54 ~~Infrared Fourier spectra (FT IR) and ^{13}C NMR were used to understand carbon~~
55 ~~chemical compositions in our biochars, and it was observed that the numbers of the~~
56 ~~shoulders representing aromatic groups, considered as stable carbon structure appeared~~
57 ~~as the temperature came closer to 600°C , as well as in FT IR. In rice materials (RS and~~
58 ~~RH), the peaks assigned to SiO_2 was observed in differentials temperature ranges of~~
59 ~~biochars (400–800 $^{\circ}\text{C}$) in FT IR along with retained small shoulder of aromatic carbon~~
60 ~~(over 1620 cm^{-1}).~~ The biochar obtained from rice materials (RH and RS) has high
61 biochar yield and the unique chemical property as a consequence of the incorporation of
62 silica element into chemical structure, while in the biochar from wood materials (AB
63 and OB) the enrichment with carbon content together with high absorption character
64 was created. We ~~propose~~suppose that the pyrolysis at 600°C creates the most
65 recalcitrant character for carbon sequestration, meanwhile the pyrolysis at 400°C
66 ~~produces the superior properties as a fertilizer by retain~~ing volatile and easily labile
67 ~~compounds~~ compounds, which promotes soil microbial activities.

68
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70 **Keywords:** biochar; pyrolysis; NMR; carbon sequestration; crop residues
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77 1. Introduction.

78 The interests in biochar utilization as a strategy for mitigation of global warming
79 is steadily are-increasing. Besides the growing attention to the biochar-utilization of
80 biochar for the-carbon sequestration, a number of works are reported on a-alternative
81 variety-of-purposesuses of biochar, such as the improvements of soil fertility, plant
82 growth and decontamination of pollutants such as pesticides, heavy metals, and
83 hydrocarbons (Beesley et al., 2011; Cabrera et al., 2011). ~~Since~~†The diverse
84 applications of biochar would be determined by its physicochemical properties, which
85 are governed by the pyrolysis conditions (heating temperature and duration) and the
86 original feedstock (Enders et al., 2012). For this reason,~~should be in accordance with the~~
87 ~~adequate ability and property each biochar has,~~ the information on the whole
88 production ~~processscheme,~~ which mostly determine fundamental biochar character, is a
89 key factor in defining any strategy for the use of biochar. to understand them. Moreover,
90 ~~Pyrolysis is the thermo-chemical process of heating biomass under low oxygen~~
91 ~~presence to produce pyrogenic material. Heating durations, temperatures, and types of~~
92 ~~feedstock materials are main components to determine the property of final product.~~
93 Pyrolysis is the thermo-chemical process of heating biomass under low oxygen presence
94 to produce pyrogenic material. Heating condition, and types of feedstock materials are
95 main components to determine the property of final product (Enders et al., 2012), and
96 the differences in stability between biochars and the transformation after adding to the
97 soil is affected by the initial property (Joseph et al., 2010). The
98 The physicochemical properties of biochar can drive changes in soil nutrient and
99 C availability and provide physical protection of microorganisms from predators and
100 desiccation, which finally promotes the alteration of the microbial diversity and the
101 taxonomy (Leehman et al., 2011). †Biochar derived from relatively low temperature

102 pyrolysis are characterized by a high content of volatile matter, containing ~~ed~~ easily
103 decomposable substrates, which can contribute ~~sed to the~~ plant growth ~~as an additional~~
104 nutrition, according to the reports (Robertson et al., 2012; Mukherjee and Zimmerman,
105 2013 ~~Lammirato et al., 2011~~). On the other hand, the structure of the biochar derived
106 from ~~the~~ high temperature pyrolysis, ~~is was refined to more selected compounds,~~
107 formed ~~characterized by~~ larger surface area and ~~also showed higher~~ aromatic carbon
108 contents, which can ~~could promote and finally this physico-chemical property promotes~~
109 the adsorption capacity for bioremediation as well as the recalcitrant character for
110 carbon sequestration (Lehmann, 2007). ~~Also, it has been considered that the yields by-~~
111 ~~products such as fuels and gases generated during the pyrolysis were influenced by~~
112 ~~pyrolysis temperature and duration~~ (Grierson et al., 2009; Mahinpey et al., 2009; Gell et
113 ~~al., 2011~~).

114 The type of feedstock material is also an important factor to guide the proper
115 orientation of application, since the properties of biochar will be affected by the nature
116 of the original material, and consequently its effect in soil. The soil cation exchange
117 capacity is enhanced more by manure-based biochars than wood
118 (~~Eucalyptus~~ Eucalyptus) biochar (Singh et al., 2010), meanwhile the treatment of the
119 soil with woodchip biochar resulted in higher saturated hydraulic conductivities than the
120 manure biochar treatment (Lei and Zhang, 2012).

121 The aim of our study is to optimize the physicochemical characteristics of
122 biochar for its use in agriculture by combining different pyrolysis conditions and the
123 selection of different agricultural wastes as feedstocks. ~~biochar production of each~~
124 different material. To achieve this aim, ~~evaluating~~ the thermo-chemical properties of
125 biochars obtained ~~derived by different feedstock with~~ at different temperature (400-800
126 °C) were evaluated. Rice husk (RH) and rice straw (RS) are used in our work as original
127 materials, since the global amounts of residues from rice crop (*Oryza sativa* L.) are 0.9

128 Gt for a year which constitutes the 25% of the total amount of whole agricultural
129 residues in the world (Knoblauch et al, 2011). Also, the research on characteristic of
130 biochars derived from orchard residues, pruning woodchips of apple tree (AB) (*Malus*
131 *pumila*), ~~are takenen conducted place, comparing with hard-wood- biocharas well as~~
132 ~~the other tree wood chip from of~~ oak tree (OB), (*Quercus serrata*). ~~According to the~~
133 ~~FAO statistics, . the 793800 metric tons of apple is produced in Japan in 2012, and 50~~
134 ~~percent of the whole production are from Aomori prefecture, which is well known as~~
135 ~~the origin of variety “Fuji Apple”. However, 36879 ton/ year (dry weight) of pruning~~
136 ~~branches in this region, which estimate more than 75% of total volume, still remains~~
137 ~~without utilization (NADO report). This is probably due to the concern that the remnant~~
138 ~~of pesticide, insecticide or fire retardant, that impregnated into the wood and finally~~
139 ~~making them psychical inseparable (Badger, 2002), is hazardous material for soil~~
140 ~~ecosystem if plowing residual orchard materials as organic amendment. The~~
141 ~~carbonization of pruning woodchip could be alternative waste management not only for~~
142 ~~reducing hazardous material such as pesticide remnant (Suri and Horio, 2010) but also~~
143 ~~for sequestrating carbon in soil. Although several works on the use of pruned-biochar as~~
144 ~~soil amendment have been ~~are~~ recently published recently for soil amendment (Fellet et~~
145 ~~al., 2011; Albuquerque et al., 2013), the evaluation of the pyrolysis during production~~
146 ~~process on this feedstock is hardly reported. The optimization of pyrolysis production~~
147 ~~should be examined by monitoring the production process.~~

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149 2. MATERIALS AND METHODS

150 2.1 Biochar preparation from agricultural residues

151 Biochars used in this work were made from two rice residues (*Oryza sativa* L.): straw
152 and husk, and two woody materials: a kind of broad-leaved trees (*Quercus serrate*
153 Murray) and apple wood chips (*Malus pumila*). All materials were first dried in air and

154 | then cut into small pieces (less than 4-5cm) to put into a ceramic vessel (370cm³) for a
155 | commercial electric furnace (SOMO-01 Isuzu, Japan), and were charred for 10 hours at
156 | different temperatures (from 400 to 800°C) with 10 °C min⁻¹ heating rate.

157

158 | 2.2 Chemical analysis of biochar

159 | After the pyrolysis process, all samples were grounded ~~to be homogenized~~, and sieved
160 | to less than 0.5 mm in diameter. The biochar yield was calculated by the proportion of
161 | the weight of pyrolysis product to the original material. The ~~determination analysis~~ of
162 | volatile matter and ash content was conducted according to the American Society for
163 | Testing and Materials (ASTM) D1752-84, which is recommended in the International
164 | ~~Biochar international organization Initiative~~ (~~www.biochar-international.org~~). The
165 | volatile matter was determined by measurement of weight loss following combustion of
166 | about 1 g of charcoal in a crucible at 950 °C. With the same procedure as the volatile
167 | matter, the ash content was determined at 750, °C. The pH of each mixture pH at 1:10
168 | (w/v) ratio was measured with a MP220 pH-meter. Micro- and meso-porosity was
169 | evaluated by the iodine (I₂) and methylene blue (MB) adsorption capacity, respectively,
170 | following the methodology used by Gaspard et al., (2007). The specific surface area was
171 | determined using N₂ sorption isotherms run on automated surface area. The specific
172 | surface areas distribution ~~reading-were as~~ taken from adsorption isotherms, using the
173 | equation of Brunauer–Emmett–Teller (BET) surface area (Zhang et al., 2011).

174 | *Elemental composition*

175 | –The elemental composition of –carbon (C), hydrogen (H), and –nitrogen (N) was
176 | determined using an Elemental analyzer (Thermo Finnigan EA-1112, Thermo Fisher
177 | Scientific Inc., Massachusetts, America), and the oxygen (O) content was determined by
178 | Vario EL cube, Elementar Analysensysteme GmbH Co.

179 | Thermal analysis

180 Thermal analysis of the biochars was measured by using a SDT-2960 simultaneous
181 DSC-TGA thermal analyzer (TA instruments) under static air atmosphere with as the
182 following temperature ramp procedure: a temperature equilibrating at 30 °C followed by
183 a linear heating rate of 5 °C min⁻¹ from 30 to 105 °C, an isotherm for 10 min and then
184 continued ramping of 5 °C min⁻¹ from 105 to 680 °C.

185 *Infrared Spectra*

186 Infrared spectra were recorded on a Varian 670-IR (Agilent Technologies Inc., CA)
187 using the pellet technique by mixing 1 mg of dried biochar with 300 mg of pre-dried
188 and pulverized spectroscopic-grade KBr (from Merck & Co., Whitehouse Station, NJ).

189 The following broad band assignation was used (Chen ~~B~~ and Chen ~~Z~~, 2009; Haslinawati
190 et al., 2011; Novak et al., 2010; Peng et al., 2011; Yuan et al., 2011; Wu et al., 2012;
191 Guo and Chen, 2014): 3400 to 3410 cm⁻¹, H-bonded O–H stretching vibrations of
192 hydroxyl groups from alcohols, phenols, and organic acids; 2850 to 2950 cm⁻¹, C–H
193 stretching of alkyl structures; 1620–1650 cm⁻¹, aromatic and olefinic C=C vibrations,
194 C=O in amide (I), ketone, and quinone groups; 1580 to 1590 cm⁻¹, COO- asymmetric
195 stretching; 1460 cm⁻¹, C-H deformation of CH₃ group; 1280-1270 cm⁻¹, O-H stretching
196 of phenolic compounds; and three bands around 460 cm⁻¹, 800 cm⁻¹ and 1000-1100
197 cm⁻¹, bending of Si-O stretching.

198 *Solid-state nucleic resonance spectroscopy (NMR)*

199 Cross-polarisation magic angle spinning (CPMAS) ¹³C nuclear magnetic resonance
200 (¹³C-NMR) spectra were acquired in the solid samples with a Varian 300, equipped with
201 a 4-mm-wide bore MAS probe, operating at a ¹³C resonating frequency of 75.47 MHz.
202 The assignation of the following peaks and broads was used (Brewer et al., 2009;
203 Calvero et al., 2011): The peak around 30 ppm, is considered as content of methylenic
204 chains and/or CH₂ groups deriving from various lipid compounds and, plant waxes, and
205 plant biopolyester; Two peaks at 55 ppm and 70 ppm, assigned to methoxy and O-alkyl

206 groups characteristic of the relatively-easily-biodegradable compounds such as
207 remaining cellulose, and hemicellulose; The broad band around 130 ppm, related to
208 alkyl substitutions in the p-hydroxy phenyl ring of cinnamic and p-coumaric units of
209 both lignin and suberin biopolymers, as well as to both partially-degraded lignin
210 structures and condensed aromatic and olefinic carbons; The sharp peak at 170 ppm,
211 assigned to a large content of carboxyl groups in aliphatic acids of plant and microbial
212 origin and/or amide groups in amino acid moieties. The spectra were integrated in the
213 chemical shift (ppm) resonance intervals of 0–45 ppm (paraffinic carbons), 46–65 ppm
214 (methoxy C from OCH₃, and complex aliphatic carbons), 66–90 ppm (O-aliphatic C,
215 such as alcohols and ethers), 91–145 ppm (aromatic carbon), 145–160 ppm (phenolic
216 carbons), 160 –185 ppm (carboxyl, amides and ester) and 185–220 ppm (carbonyls)
217 (Wang et al., 2007; Zhang et al., 2012+).

218

219 3. Result and Discussion

220 3.1. Physicochemical characteristics of biochar

221 The characteristics of biochars originated from different agricultural wastes materials
222 are shown in Table 1. ~~Lower~~ temperature pyrolysis ~~process, has produced a~~ higher
223 biochar yield and ~~an more~~ enriched volatile matter composition than the high
224 temperature biochars inside biochar product. ~~The volatile compounds are easily~~
225 ~~degradable compounds, which stimulates the activity of microorganisms in soil as~~
226 ~~substrate and ends up supplying plant nutrition (Steinbess et al., 2009; Zimmerman,~~
227 ~~2012).~~ The biochar yields and volatile contents were gradually reduced by increasing
228 pyrolysis temperatures. ~~Not only the range of pyrolysis temperature~~ Moreover, the type
229 of feedstock also affected biochar yields and the volatile matter content. Among
230 different biochar types, ~~two types of~~ woody biochars (AB and OB) showed larger
231 variation in volatile content from low temperature to high temperature (from 400 °C to

232 800 °C) than non-woody biochars (RS and RH), as observed by , and this result is in
233 accordance with other report (Enders et al., (2012)). These authors found that the ex
234 mention that this attributes to the recalcitrant character of lignin in woody feedstocks
235 can partially resist , which resists still partially pyrolytic decomposition at 400 °C, but
236 not in the range of 950 °C (used for the determination of ash content), increasing the
237 volatile content of woody biochar prepared a relatively low temperatures. for
238 determinating the volatile content quantification. low yields and low volatile contents
239 compared to other two kinds of biochar from rice residues (RS and RH). Also, wood
240 original biochar (AB and OB) has less ash content than others, (RS and RH), which is in
241 the accordance with the work of Singh et al., (2010). The biochars derived from rice
242 material (RS and RH) have a high ash content in all temperature ranges, which may
243 have casued and the partial change in of the structure and composition by a possible
244 interaction between organic and inorganic constituents during feedstock pyrolysis, as
245 already reported by composition partially could be occurred according to the report
246 (Elders et al., (2012), in biochar that the biochars, containing above 20% of ashesed
247 greater than 20% ash, could be possible interaction between organic and inorganic
248 constituents during feedstock pyrolysis. Overall, tThose results might be due to the
249 differences in compositions of the original agricultural material since rRice plants are
250 enriched with Si, which strongly relates to the ash content of the biochar (Mukome et al.,
251 2013) by the formation of Si-C bonds which increases the aromatic components and
252 recalcitrance of the biochars with increasing pyrolysis temperatures (Guo and Chen,
253 2014) while. In the case of woody feedstocks, , while recalcitrant carbons such as lignin
254 content are predominantly contained in woody plants (Liu and Zhang, 2009; Spokas et
255 al., 2009; Joseph et al., 2013). It is reported that the bonds Si-C is probably take part in
256 cross linking of organic and inorganic compounds such as aromatic groups or

257 ~~crystallites, and the higher temperature that biochar production is taken place, the SiO₄~~
258 ~~is more dominant relative to SiO₂ (Lehmann et al., 2011).~~

259 The pH values increased ~~with by higher~~ temperature, probably as a consequence
260 ~~of resulted from~~ the relative concentration of non-pyrolysed inorganic elements, already
261 present in the original feedstocks (Novak et al., 2009). The porosity and surface area
262 represent the main physical properties of biochar, which are and strongly connected
263 ~~strongly~~ with the improvement of soil properties such as soil adsorption capacity, and
264 water retention abilities, ~~which those has could potential to improve soil property~~
265 (Kalderis et al., 2008), ~~and in particular, taking the advantage of enhanced these~~
266 ~~properties; T~~he number of works on the application of biochar derived from the rice
267 husk has ~~ve~~ been reported ~~to on enhancement of these properties in for improvement of~~
268 the soil quality (Kalderis et al., 2008; Liu and Zhang, 2009; Lei and Zhang, 2013). As
269 shown in Table 1, the biochar production ~~withat~~ higher temperatures generally enlarged
270 methylene blue number, I₂ absorption, and surface area, compared to than the
271 production ~~withat~~ lower temperature ($p < .001$), and these results are in accordance with
272 other previous work (Gaskin et al., 2008; Liu and Zhang, 2009; Yu et al., 2011).

273 Regarding of comparison among the variety of origins, the difference in micro-porosity
274 (I₂) of biochars between from wood feedstock (AB and OB) and from rice residues (RH
275 and RK) was gradually enlarged as increasing pyrolysis temperature from 500°C to
276 800°C. In contrast, an apparent difference in surface area was observed. The surface
277 areas of RH and RK reduced at 800°C, while those of AB and OB still had been
278 extending. These decreases in surface areas of RH and RK will be attributed to ash
279 content in biochar, that high content of inorganic ash in biochar filled or blocked access
280 to micropores, resulting in relatively low surface area (Mackay and Roberts, 1982; Song
281 and Guo, 2012).

282 3.2. Analytic elements

283 Analytical elements and both ratios of H/C and O/C are also indicators to evaluate
284 the characters of biochars (Nguyen and Lehmann, 2009). As shown table 2, it is
285 observed that the increasing temperature results in loss of hydrogen and oxygen than
286 carbon. Dehydrogenation of CH₃ on biochar properties as consequence of thermal
287 induction is the indicative of changes in biochar recalcitrance (Harvey et al., 2012).
288 Concerned with oxygen loss, the biomass material normally comprises of labile and
289 recalcitrant O fractions; a labile O fraction that is quickly lost upon initial heating, and a
290 recalcitrant O fraction which retained in the char of final product (Rutherford et al.,
291 2013).

292 Regarding with the H/C/ and O/C, Table 2 shows the ~~redaction~~ reduction in these
293 ratios with charring temperature, being attributed to the dehydration and
294 decarboxylation reactions. The change of O/C ratio in the range from 400 °C to 500 °C
295 was remarkably observed in the order of RS>RK> AB> OB. ~~It is reported~~ (Yang et al.,
296 (2007) and ~~Khodadad et al.,(2011)~~ ~~found~~ that biochar made from wood and at higher
297 temperatures are less biologically labile, containing relatively higher proportions of
298 more aromatic organic matter, compared to other ~~biochars original materials of prepared~~
299 ~~from~~ agricultural residues and at lower temperature. As shown in the van Krevelen
300 diagram (Fig. 1), the constancy of the reduction in the H/C and O/C ratios as increasing
301 temperature are observed, reflecting the loss of easily degradable carbon compounds
302 such as volatile matters.- At the parallel, lower C/O ratio in biochar with higher
303 temperature indicate the arrangement of aromatic rings (Spokas et al., 2010), forming
304 crystal graphite-like structure with high stability (Wu et al., 2012; Dong et al., 2013).

305 Concerning with the difference of the feedstocks in the diagram, the rice material
306 biochars (RS and RH) wereas distanced from Y axe at 600 °C and 700°C;
307 wheraswhereas the stable reduction of the H/C and O/C in wood biochars (AB and OB)
308 was shown. This result was mainly due to the decrease of C content in RS and RH from

309 ~~500⁰C to 600⁰C, which the shift moved from 45.2% to 40.3% and from 37.5% to 33.8%,~~
310 ~~in RS and RH, respectively (Table 2).~~ The reduction of carbon content in biochar
311 production could be related to the chemical and physical composition. The change of
312 the physical and structural composition of rice straw biochar between the pyrolysis
313 condition of 500⁰C and 700⁰C is reported by Guo and Chen, (2014)-, using SEM-EDS
314 images. For the rice husk biochar made at 500⁰C , the silicon was associated with
315 carbon and formed a dense structure, forming Si-encapsulated carbon, meanwhile the
316 silicon component were physically distanced from carbon structure in biochars prepared
317 at the highest temperature for the other made at (700⁰C).

318

319 3.3. Thermal analysis

320 Thermal analysis is a useful method to understand -the structure of biochar materials.
321 (Kalderis et al., 2014; Mimmo et al., 2014). In our study (Fig. 2), all biochar samples
322 had a similar of the thermal degradation profile, with an increasing weight loss with
323 increasing pyrolysis temperature. ~~has same tendency that biochar produced at 400⁰C~~
324 ~~has the largest proportion of lost weight. The difference among the feedstocks (wood v.s.~~
325 ~~no-wood) was observed in the total weight losses, as observed in the ash~~
326 ~~content.~~ location of the curve of lost weight. The curves of the lost weight in AB and OB
327 ~~were reached up to to a great extent until the 910 percent of total weight, meanwhile the~~
328 ~~curve in RH and RK reached were stopped around half volume of weight (40-50%),~~
329 ~~reflecting the higher mineral content .This would be reflected to the high mineral~~
330 ~~content in rice material, and moreover during charring process this mineral content~~
331 ~~performs as a barrier to prevent from heat diffusion and the release of the volatile~~
332 ~~contents (Xu and Chen, 2013).~~

333

334 3.4. Chemical composition with spectra parameters (FT-IR and NMR)

335 | The FT-IR is a great tool ~~to shed on the light to understand~~ to observe the shift
336 | change of chemical composition. The aliphatic loss process is represented by the band
337 | of FT-IR with aliphatic C-H stretching ($2950\text{-}2850\text{cm}^{-1}$) at increasing temperature from
338 | 400°C to 600°C ~~–(Figure 2)~~, meanwhile ~~thea couples of~~ representative peaks for
339 | aromatic carbon appeared more clearly such as C-H stretching ($750\text{-}900\text{cm}^{-1}$ and 3050-
340 | 3000cm^{-1}), C=C ($1380\text{-}1450\text{ cm}^{-1}$), C-C and C-O stretching ($1580\text{-}1700\text{cm}^{-1}$). As
341 | shown by the infrared spectra, charring temperature modifies the functional group, and
342 | thus aliphatic C groups decrease but aromatic C increases (Lee et al., 2010). Since
343 | longevity of biochar is a matter of debate in relation with the biochar production
344 | (Nguyen and Lehman, 2009; Peng et al., 2011), the pyrolysis process of 600°C , which
345 | creates more recalcitrant character by increasing aromatic compounds, has suitable
346 | method in terms of the carbon sequestration. However, ~~-~~ when the charring temperature
347 | increase over 700°C and 800°C , the intensity of bands decline gradually such as
348 | hydroxyl group ($3200\text{-}3400\text{ cm}^{-1}$) and even aromatic bands ($1580\text{-}1600\text{cm}^{-1}$ and 3050-
349 | 3000cm^{-1})~~–~~. Other works (Yuan et al., 2011) report that the number of bounds
350 | representing functional groups are present at the lower-temperature biochars (300°C and
351 | 500°C), and are absent in the biochar-derived by 700°C . ~~The loss of these functional~~
352 | ~~groups decrease recalcitrant character of biochar, which will be hardly remained after~~
353 | ~~applying it to soil.~~

354 | The characteristic of feedstock type of biochar has been reflected by the presence of
355 | bounds ~~s~~ around 460 cm^{-1} , 800 cm^{-1} , and $1040\text{-}1100\text{cm}^{-1}$, assigned to SiO_2 , and ~~these is~~
356 | bands ~~s~~ was shown in all biochars originated from rice materials (RH and RS), showing
357 | in the Fig. 3. ~~ba. The SiO_2 is a major component in chemical structure of rice material,~~
358 | ~~and is typical of recalcitrant property. In plant physiology, the presence of silica is~~
359 | ~~knowingly found as principal component of plant phytoliths and it functions for~~

360 protection of the plant carbon from degradation (Wilding et al., 1969, Parr, 2006).
361 Furthermore, In fact, the SiO_2 is a major component in chemical structure of rice material.
362
363 In addition, not only the peak of SiO_2 , (The shoulder observed around the 1600 cm^{-1} , in
364 rice biochars (RH and RS), -which assigned to the aromatic compounds, respectively,
365 are still retained in RH and RS biochar until the 800°C biochar production.
366 Guo and Chen (2014) proposed that a novel framework of silicon-and-carbon-couple
367 can contribute a new perspective for evaluating the biochar stability, besides recalcitrant
368 character derived from aromatic carbon compounds. They mention that the structure of
369 encapsulated carbon by silica could protect the biochar against physical and chemical
370 oxidation, and presumably leads to a longer turnover time in soils.

371 The ^{13}C NMR spectra of different biochars are shown in Fig. 34 (a and b) with
372 similar shape for all biochar materials, dominated by the presence of condensed
373 aromatic signal at 127 ppm. Furthermore, this signalthe signal was observed more
374 clearly in all different biochars which are produced at 600°C , and the sharpness of this
375 peak was gradually weaken as temperature increased above~~goes away from~~ 600°C .
376 Same trend was shown in the shoulder of methoxyl carbons of lignin and carboxylic
377 carbon, at 57 ppm and 190 ppm, respectively. Especially, the biochars, made from rice
378 straw at 800°C (Fig. 3, b) demonstrated the decomposition of shoulder of these ranges.
379 From this result as well as shown in FT-IR figure, it worth of noting that there is no
380 much need to produce biochar with very high temperature (700°C and 800°C) for
381 preserving stability character ,based on the predominance of aromatic structure and
382 keeping higher chemical property with functional groups.

383 Concerning with lower temperature, the shoulder at around 20 ppm, assigned to
384 easily degradable carbon, appeared in the 400°C -produced biochars, and this shoulder
385 was eliminated in the biochar produced at 500°C . This accords with other's work

386 (McBeath et al., 2013) that biochar, produced at 300⁰-400⁰C, exhibited broad alkyl
387 signals and carbohydrate band, meanwhile these bands were not detectable over 400⁰C.
388 As shown in previous section, the biochar, produced at lower temperature, has higher
389 volatile carbon contents. The type of easily degradable compounds possibly contributes
390 to microorganisms in soil as substrate (Khodadad et al., 2011). In this sense, lower
391 temperature is suitable for the biochar utilization for soil fertility. On the contrary,
392 higher temperature pyrolysis selects functional groups and provides aromatic
393 predominant presence in chemical composition, consequently resulting to the formation
394 of recalcitrant structure. However, it should be highlighted that the excess of the high
395 temperature such as 700 °C and 800 °C is not likely suitable and efficient for biochar
396 production, since those biochars reduce recalcitrant character by heat degradation of
397 functional group, and yield lower the biochar production than other biochars.

398

399 4. Conclusion

400 In conclusion, the temperature of pyrolysis ~~process~~ and the type of feedstock
401 ~~change-drive~~ the physic-chemical properties of biochar. In our study, lower temperature
402 pyrolysis has volatile content and ash compounds retained inside biochar structure.
403 Increasing high temperature ~~re~~ re ~~pyrolysis process produces more~~ enhanced the physical
404 property of adsorption property such as large surface area and porosity and the
405 recalcitrant chemical character, reinforced by the function group, are improved. This
406 alteration was strongly shown in wood material biochar (AB and OB). By contrast, rice
407 material biochar (RH and RS) has higher biochar yield during the pyrolysis process than
408 AB and OB, and the property of the biochar product is different from wood material in
409 that the inorganic components is combined with organic moieties in related with the
410 carbon encapsulation by silicon presence. recalcitrant character of functional group and
411 adsorption property due to large surface area and porosity. By contrast, lower

412 ~~temperature pyrolysis has volatile carbon compounds retained inside biochar structure,~~
413 ~~which can induce microbial activities in soil.~~ The over-heat production (>above 600 °C)
414 showed the disappearance of the functional groups, driven by heat degradation.

415

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418

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658

Table 1. Physical and chemical characteristics of the biochars from different feedstocks; AB (apple tree branch), OB (oak tree), RH (rice husk), and RS (rice straw).

samples	temperature (°C)	Biochar Yield (%)	<u>Ash Content (%)</u>	Volatile Content (%)	pH (H ₂ O)	Methylene Blue (mg/g DW)	I ₂ adsorption (mg/g DW)	BET Surface Area (m ² /g)
AB	400	28.3	<u>4.4 ± 0.0</u>	32.436 ± 0.105	7.02 ± 0.08	4.436 ± 0.24	45.044.96 ± 2.64	11.90
	500	16.7	<u>6.5 ± 0.0</u>	18.327 ± 0.328	9.64 ± 0.07	12.04 ± 0.438	97.987 ± 2.765	58.60
	600	16.6	<u>7.6 ± 0.1</u>	11.107 ± 0.20	10.04 ± 0.02	5.765 ± 0.439	122.105 ± 1.53	208.769
	700	15.8	<u>8.0 ± 0.0</u>	7.72 ± 0.10	10.03 ± 0.02	10.63 ± 0.767	208.328 ± 1.50	418.766
	800	15.5	<u>8.6 ± 0.0</u>	6.82 ± 0.107	10.02 ± 0.02	51.879 ± 0.658	298.54 ± 1.70	545.43
OB	400	35.8	<u>3.6 ± 0.0</u>	32.106 ± 0.105	6.43 ± 0.04	3.90 ± 0.328	38.766 ± 0.04	5.60
	500	28.6	<u>5.1 ± 0.1</u>	19.42 ± 0.327	8.10 ± 0.12	5.659 ± 0.547	91.74 ± 0.106	103.247
	600	22.0	<u>5.54 ± 0.0</u>	12.30 ± 0.04	8.85 ± 0.07	5.54 ± 0.439	131.327 ± 1.547	288.658
	700	20.0	<u>6.2 ± 0.0</u>	8.328 ± 0.107	9.54 ± 0.00	17.106 ± 0.246	212.879 ± 0.109	335.64
	800	19.1	<u>8.3 ± 0.2</u>	7.987 ± 0.106	9.68 ± 0.03	29.438 ± 0.547	250.328 ± 1.40	398.245
RH	400	48.6	<u>35.9 ± 0.1</u>	22.00 ± 0.13	6.84 ± 0.03	2.94 ± 0.875	44.107 ± 1.655	193.70
	500	42.4	<u>46.2 ± 0.2</u>	10.656 ± 0.14	8.99 ± 0.04	9.72 ± 0.437	75.438 ± 1.658	262.00
	600	37.3	<u>52.8 ± 0.4</u>	6.02 ± 0.327	9.41 ± 0.00	13.50 ± 0.24	669.08.95 ± 3.13	243.00
	700	32.8	<u>55.1 ± 0.2</u>	3.985 ± 0.14	9.52 ± 0.02	13.88.9 ± 10.099	121.02 ± 1.658	256.00
	800	32.0	<u>62.6 ± 0.3</u>	3.247 ± 0.249	9.62 ± 0.01	34.106 ± 0.34	174.40 ± 3.107	295.657
RS	400	39.3	<u>34.0 ± 0.2</u>	22.42 ± 0.109	8.62 ± 0.03	29.32 ± 2.40	74.766 ± 2.64	46.60
	500	32.6	<u>43.5 ± 0.2</u>	12.80 ± 0.14	9.82 ± 0.01	29.658 ± 2.84	95.94 ± 1.52	59.94
	600	23.4	<u>58.6 ± 0.1</u>	8.436 ± 0.03	10.19 ± 0.01	33.765 ± 4.93	85.657 ± 1.658	129.00
	700	18.4	<u>69.9 ± 0.4</u>	5.33 ± 0.13	10.39 ± 0.03	40.545 ± 3.02	100.655 ± 1.52	149.00
	800	18.3	<u>73.9 ± 0.1</u>	4.547 ± 0.245	10.47 ± 0.04	82.64 ± 2.02	190.24 ± 1.34	256.976

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Table 2. The elemental compositions of biochars from different feedstocks; AB (apple tree branch), OB (oak tree), RH (rice husk), and RS (rice straw).

samples	temperature (°C)	C* (%)	H* (%)	N* (%)	O (%)	O/C	H/C
AB	400	70.218 ± 0.215	4.13 ± 0.01	0.76 ± 0.00	20.656 ± 0.12	0.22	0.71
	500	79.12 ± 0.00	2.65 ± 0.09	0.34 ± 0.01	12.011.98 ± 0.10	0.11	0.40
	600	81.546 ± 0.105	1.96 ± 0.02	0.46 ± 0.00	13.63 ± 0.326	0.12	0.29
	700	82.326 ± 1.439	1.21 ± 0.05	0.41 ± 0.02	16.34 ± 0.768	0.15	0.18
	800	84.84 ± 0.108	0.60 ± 0.01	0.34 ± 0.01	5.81 ± 0.03	0.05	0.08
OB	400	70.52 ± 0.24	3.70 ± 0.02	0.69 ± 0.02	21.547 ± 0.215	0.23	0.63
	500	77.657 ± 0.34	2.51 ± 0.16	0.51 ± 0.03	17.73 ± 0.545	0.17	0.39
	600	81.22 ± 0.548	1.92 ± 0.01	0.48 ± 0.02	16.015.96 ± 0.215	0.15	0.28
	700	83.22 ± 0.23	1.16 ± 0.06	0.31 ± 0.00	15.014.97 ± 0.107	0.13	0.17
	800	82.985 ± 0.42	0.69 ± 0.06	0.32 ± 0.00	17.329 ± 0.12	0.16	0.10
RH	400	44.659 ± 0.326	2.50 ± 0.00	0.69 ± 0.02	16.32 ± 0.23	0.27	0.67
	500	45.215 ± 0.33	1.27 ± 0.03	0.47 ± 0.02	7.12 ± 0.216	0.12	0.34
	600	40.435 ± 0.74	0.85 ± 0.05	0.37 ± 0.01	9.23 ± 0.31	0.17	0.25
	700	38.81 ± 0.546	0.46 ± 0.04	0.26 ± 0.02	12.769 ± 0.20	0.25	0.14
	800	40.41 ± 0.768	0.28 ± 0.01	0.22 ± 0.00	2.769 ± 0.01	0.05	0.08
RS	400	49.92 ± 0.215	2.80 ± 0.12	1.22 ± 0.01	12.02 ± 0.106	0.18	0.67
	500	37.548 ± 0.22	0.93 ± 0.03	0.61 ± 0.01	8.64 ± 0.33	0.17	0.30
	600	33.878 ± 1.02	0.60 ± 0.07	0.41 ± 0.04	13.768 ± 0.32	0.30	0.21
	700	36.326 ± 0.879	0.51 ± 0.06	0.34 ± 0.02	17.438 ± 0.94	0.36	0.17
	800	29.217 ± 0.437	0.25 ± 0.02	0.25 ± 0.01	3.71 ± 0.01	0.10	0.10

Figure legends

Fig.1- Van Krevelen diagram of biochar originated from different feedstock; AB (apple tree branch), OB (oak tree), RH (rice husk), and RS (rice straw). Each symbol shows pyrolysis temperature as follows; Black =8000C, Gray = 7000C, Line= 6000C Dot = 5000C, and White= 4000C.

Fig. 2. a. - Thermal analysis of biochars of wood materials; AB (apple tree) and OB (oak tree)

Fig.2. b. - Thermal analysis of biochars of of rice residues; RH (rice husk) and RS (rice straw)

Fig. 3.a. - FT-IR spectra of biochars of wood materials; AB (apple tree) and OB (oak)

Fig .3.b. - FT-IR spectra of biochars of rice residues; RH (rice husk) and RS (rice straw)

Fig. 4. a. - ¹³C CPMAS-NMR of biochars of wood materials; AB (apple tree) and OB (oak tree)

Fig.4. b. - ¹³C CPMAS-NMR of biochars of rice residues; RH (rice husk) and RS (rice straw)

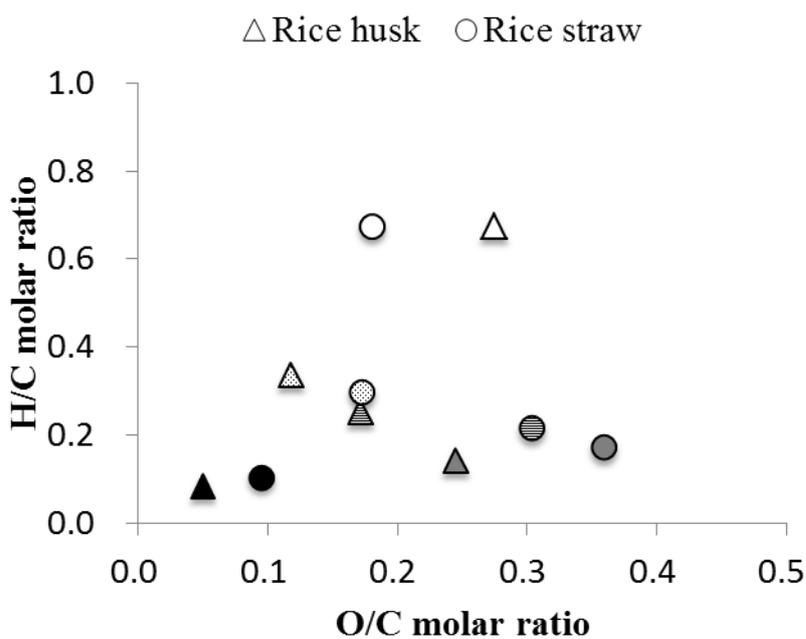
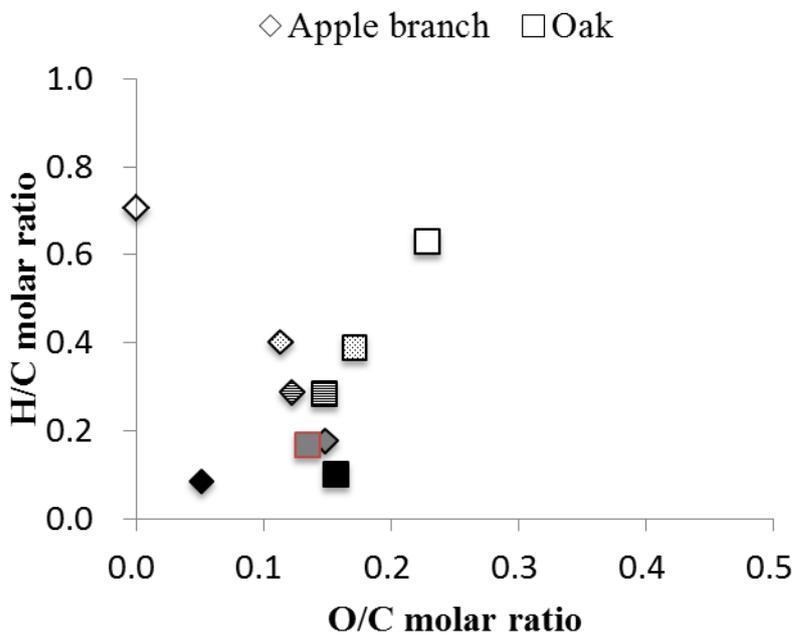


Fig. 1 Van Krevelen diagram of biochar originated from different feedstock. The temperature range of pyrolysis process is as following; Black = 800°C, Gray = 700°C, Line = 600°C, Dot = 500°C, and White = 400°C

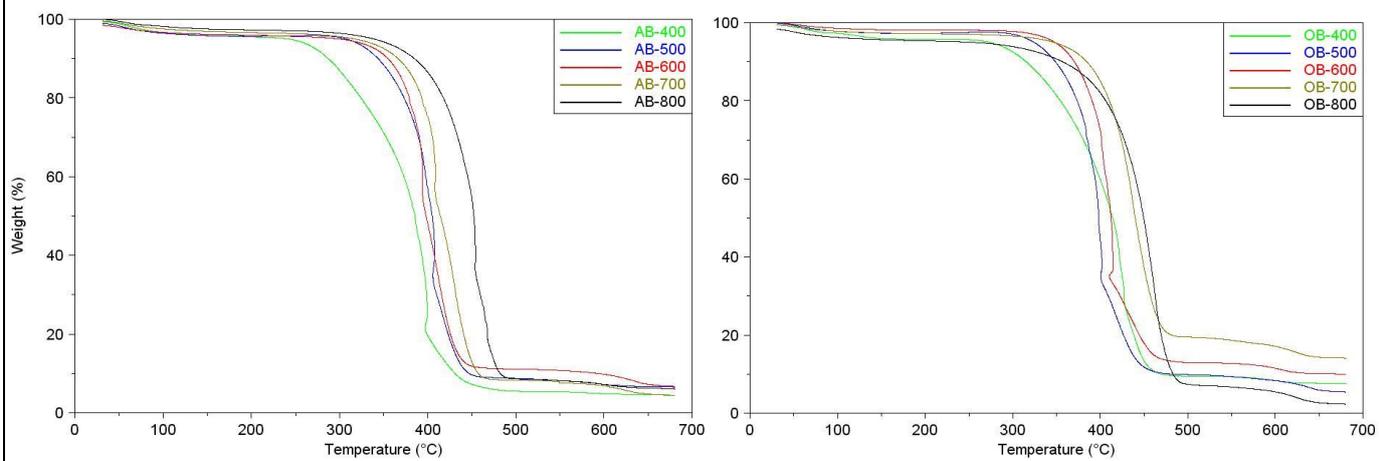


Fig. 2.a.-Thermal analysis of biochars of wood materials; AB (apple tree) and OB (oak tree)

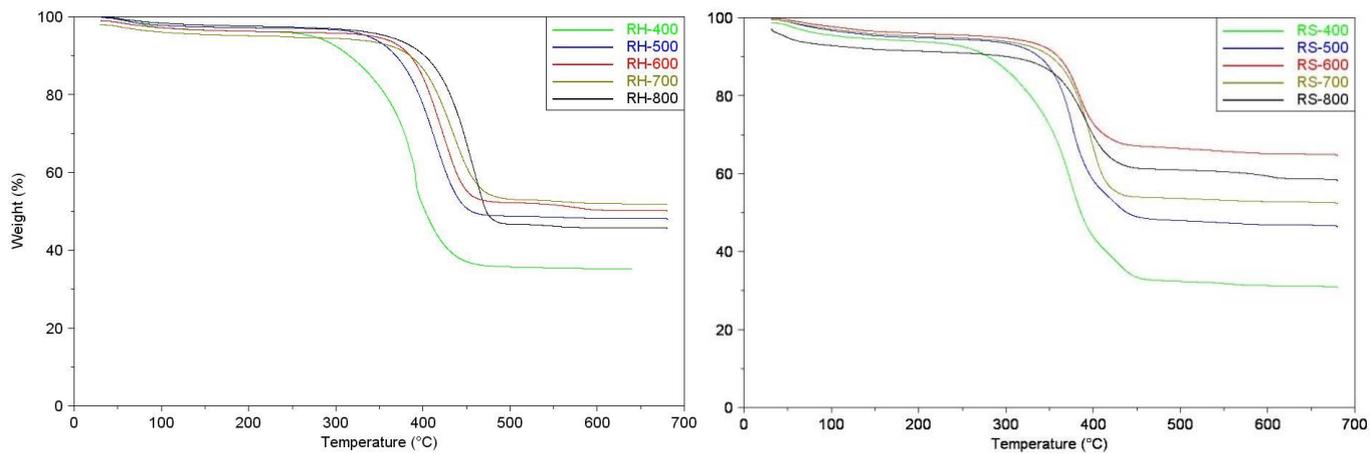


Fig.2. b. - Thermal analysis of biochars of of rice residues; RH (rice husk) and RS (rice straw)

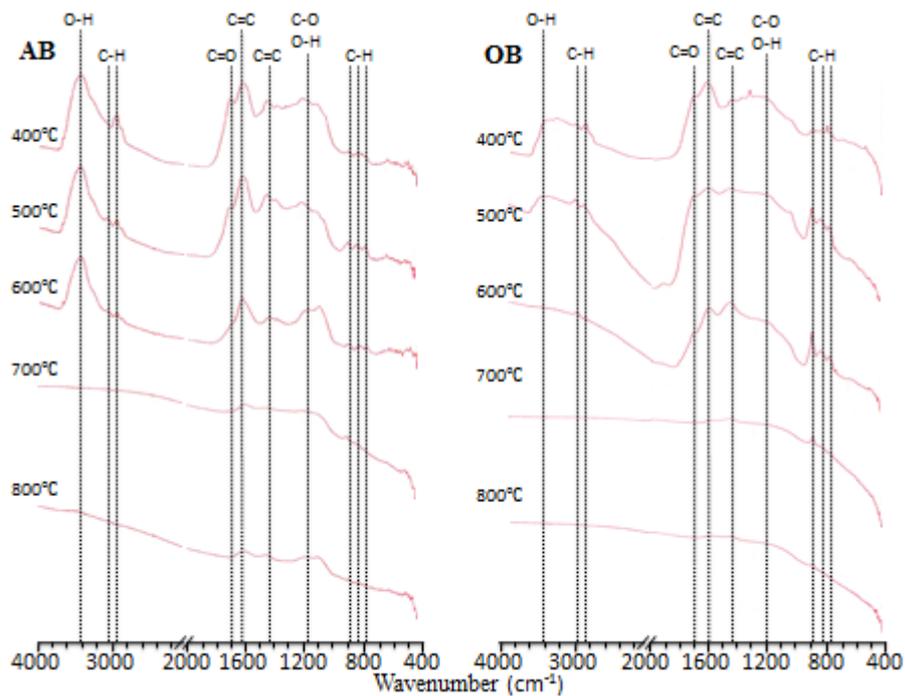


Fig. 32.a.-FT-IR spectra of biochars of wood materials; AB (apple tree) and OB (oak tree)

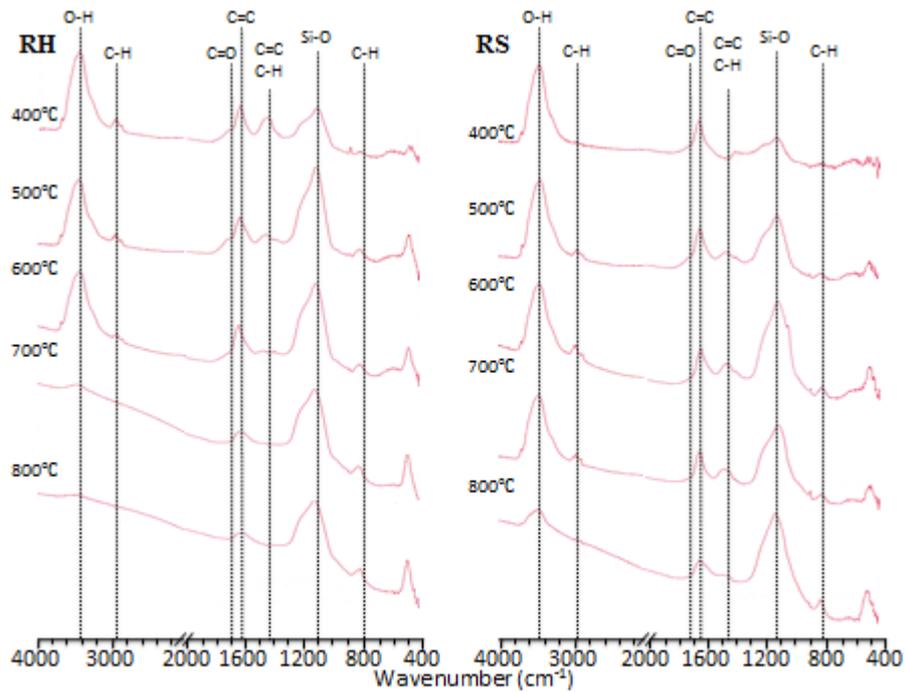


Fig. 32.b.- FT-IR spectra of biochars of rice residues; RH (rice husk) and RS (rice straw)

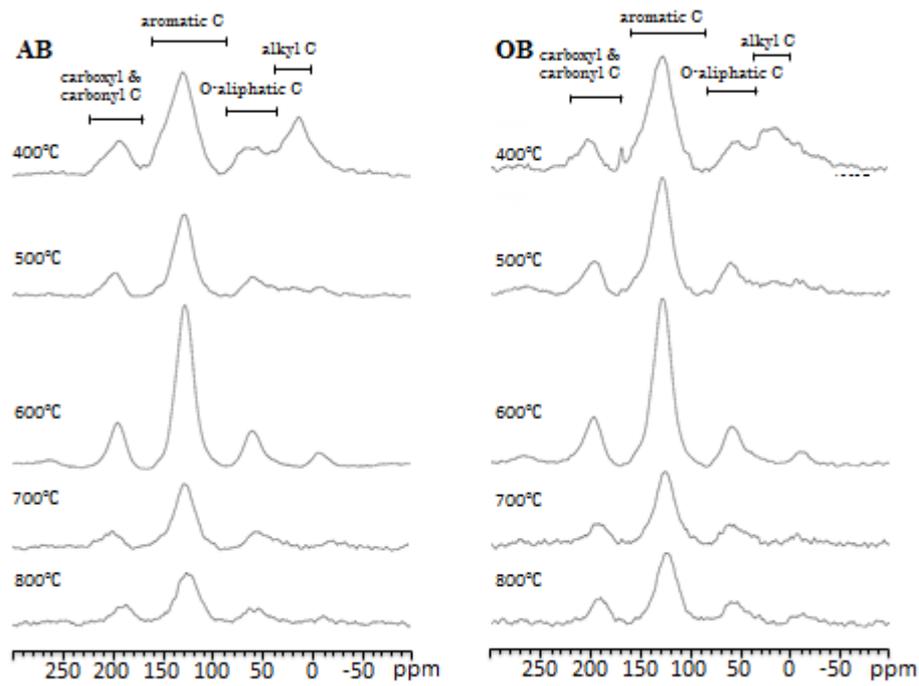


Fig. 43. a. ^{13}C CPMAS-NMR of biochars of wood materials; AB (apple tree) and OB (oak tree)

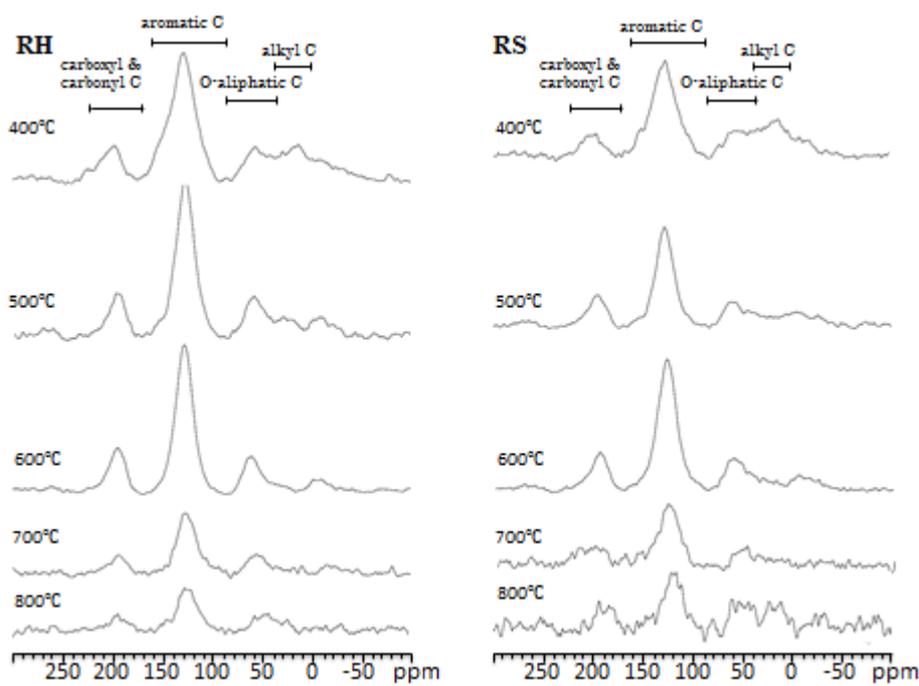


Fig. 43. b. ^{13}C CPMAS-NMR of biochars of rice residues; RH (rice husk) and RS (rice straw)

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TITLE OF THE PAPER

Physical and Chemical Characterizations of biochars derived from different agricultural residues

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1 | **Physical and Chemical Characterizations of Biochars Derived from Different**
2 | **Agricultural Residues**

3
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25

26 **Abstract**

27 Biochar ~~has been evaluated globally~~ is widely recognized as an efficient tool for
28 carbon sequestration and soil fertility. The understanding of ~~the-its~~ chemical and
29 physical properties ~~of biochar~~, which are strongly related to the type of the initial
30 original material used and pyrolysis conditions, is ~~an important~~ crucial ~~key~~ to identify
31 the most suitable ~~use~~ application of biochar in soil. A selection of organic wastes with
32 contrasting characteristics (e.g., rice husk, rice straw, wood chips of apple tree (*Malus*
33 *pPumila*), and oak tree (*Quercus serrata*)) were pyrolyzed at different temperatures
34 (400, 500, 600, 700, and 800 °C) in order to optimize the physicochemical properties of
35 biochar as a soil amendment. Low-temperature ~~p~~Pyrolysis ~~at low temperatures~~ produced
36 high biochar yields; in contrast, ~~but~~ ~~high~~ ~~temperature~~ pyrolysis led to ~~produced~~
37 biochars with a high C content, large surface area, s and suitable adsorption
38 characteristics. ~~The~~ biochar obtained from rice materials (RH and RS) ~~has showed a~~
39 high ~~biochar~~ yield and ~~the~~ unique chemical properties as a consequence because of the
40 incorporation of silica elements into its chemical structure, ~~while in~~ ~~T~~the biochar
41 obtained from wood materials (AB and OB) showed high ~~the enrichment with~~ carbon
42 content ~~together and with~~ high absorption character ~~was created~~. We suggest
43 ~~propose~~ that ~~the~~ pyrolysis carried out at 600 °C ~~creates~~ leads to ~~the most~~ a high
44 recalcitrant character (suitable for carbon sequestration), ~~meanwhile~~ ~~whereas that~~ ~~the~~
45 ~~pyrolysis~~ at 400 °C produces ~~retains~~ volatile and easily labile compounds.

46

47

48 **Keywords:** biochar; pyrolysis; NMR; carbon sequestration; crop residues

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55 **1. Introduction:**

56 The interest in the application of biochar ~~utilization~~ as a strategy method for
57 mitigat~~ing~~on of the global-warming effects is steadily increasing. Besides the studies
58 about the growing attention to the utilization use of biochar for carbon sequestration, a
59 number of works-reports have focused are reported on its alternative uses-applications
60 of biochar, such as for the improvement of soil fertility and, plant growth and
61 decontamination of pollutants such as ~~such as~~ pesticides, heavy metals, and
62 hydrocarbons (Beesley et al., 2011; Cabrera et al., 2011). The diverse range of biochar
63 applications of biochar would depends be determined by on its physicochemical
64 properties, which are governed by the pyrolysis conditions (heating temperature and
65 duration) and the original feedstock (Enders et al., 2012). ~~For this reason~~ Thus, detailed
66 the information on about the complete whole production process processis is a key factor
67 in defining the most suitable in defining any application strategy for the use of biochars.

68

69 The biochar physicochemical properties of biochar can drive-cause changes in
70 the soil nutrient and C availability, and and provide physical protection of to
71 microorganisms from-against predators and desiccation; this may, which finally
72 promotes the alteration of the microbial diversity and the taxonomy of the soil (Lehman
73 et al., 2011). The b Biochar derived from-from relatively low-temperature pyrolysis are
74 is characterized by a high content of volatile matter that, contain~~ing~~ing easily
75 decomposable substrates, which can contribute-support to plant growth (Robartson et al.,
76 2012; Mukherjee and Zimmerman, 2013). ~~On the other hand~~ In contrast, the structure of
77 the biochar derived from high-temperature pyrolysis is characterized by a large surface
78 area and high aromatic-carbon content, which could-may promoteincrease the

79 adsorption capacity (~~-a desirable property~~ for bioremediation) as well as the recalcitrant
80 character (~~for carbon sequestration~~) (Lehmann, 2007).

81 The type of feedstock material is ~~also another an~~ important factor ~~that~~
82 ~~determines the final application of the biochar and its effect in soil, to guide the proper~~
83 ~~orientation of application, because its since the~~ properties ~~are of~~ biochar will be
84 affected by the nature of the original material, ~~and consequently its effect in soil. For~~
85 ~~instance, t~~The soil cation~~_~~exchange capacity ~~of is enhanced more by~~ manure-based
86 biochars ~~is higher than that of than~~ wood (*Eucalyptus*) biochar (Singh et al., 2010),
87 ~~meanwhile while~~ the treatment of ~~the~~ soil with woodchip biochar result~~ed~~ in higher
88 saturated hydraulic conductivities than ~~th~~~~at treated with e~~ manure~~_~~based biochar
89 ~~treatment~~ (Lei and Zhang, 2012).

90 The aim of our study is to optimize the physicochemical characteristics of
91 biochar for its use in agriculture by ~~combining investigating~~ different pyrolysis
92 conditions and ~~the selection of different~~ agricultural wastes ~~used~~ as feedstocks. To
93 achieve this aim, the thermo-chemical properties of ~~the~~ biochars obtained ~~at~~ different
94 temperatures (400~~_~~800 °C) were evaluated. Rice husk (RH) and rice straw (RS) ~~are~~
95 ~~were~~ used ~~in our work as~~ original ~~the starting~~ materials, ~~since because~~ the global
96 amounts of residues from rice crops (*Oryza sativa* L.) ~~are is~~ 0.9 Gt ~~for per a~~ year, ~~i.e.,~~
97 ~~which constitutes the~~ 25% of the total amount of ~~the whole global~~ agricultural residues
98 ~~produced in the world~~ (Knoblauch et al, 2011). ~~More Also, the r~~research ~~is being~~
99 ~~conducted on the properties of e~~characteristic ~~of~~ biochars derived from orchard residues
100 ~~and~~, pruning woodchips of apple tree (AB) (*Malus pumila*), ~~than are taking place,~~
101 ~~comparthat on ing with~~ hard-wood biochar ~~derived from the of~~ oak tree (OB); (*Quercus*
102 *serrata*). The carbonization of pruning woodchip ~~could may~~ be ~~considered as an~~
103 alternative waste management not only for ~~the reduction of ing~~ hazardous materials~~s~~
104 such as pesticide remnant (Suri and Horio, 2010) but also for ~~soil sequestering~~ carbon

105 ~~sequestration in soil~~. Although several ~~works studies have been recently proposed on~~ the
106 use of pruned-biochar as ~~a~~ soil amendment ~~have been recently published~~ (Fellet et al.,
107 2011; Albuquerque et al., 2013), ~~the reports on the~~ evaluation of the pyrolysis process
108 on this feedstock ~~are is hardly scant reported~~.

110 2. ~~Materials and Methods~~ **ATERIALS AND METHODS**

111 2.1 Biochar ~~P~~preparation from ~~A~~gricultural ~~R~~esidues

112 ~~The -b~~Biochars used in this work were ~~obtained made~~ from two rice residues (*Oryza*
113 *sativa* L.), ~~e.g.:~~ straw and husk, ~~as well as;~~ and two woody materials, ~~e.g.:~~ a ~~type of~~
114 ~~kind of~~ broad-leaved trees (*Quercus serrate* Murray) and apple ~~--~~ wood chips (*Malus*
115 *pumila*). All materials were first dried in air and then cut into small pieces (less than 4 ~~--~~
116 5 cm); ~~these were then inserted into -to put into-~~ a ceramic vessel (370 cm³) ~~that was~~
117 ~~used in for-~~ a commercial electric furnace (SOMO-01 Isuzu, Japan). ~~This -and were was~~
118 charred for 10 ~~hours~~ at different temperatures (from 400 to 800 °C) ~~with at a heating~~
119 ~~rate of 10 °C min⁻¹ -heating rate.~~

121 2.2 Biochar Chemical ~~A~~analysis ~~of biochar~~

122 -After the pyrolysis process, all samples were ~~grounded~~ and sieved to less than 0.5 mm
123 in diameter. The biochar yield was calculated ~~by as~~ the proportion of the weight of
124 pyrolysis product to the original material. The determination of ~~the~~ volatile matter and
125 ash content was conducted according to the American Society for Testing and Materials
126 (ASTM) D1752-84, which is recommended ~~in by~~ the International Biochar Initiative.
127 The volatile matter was ~~thus~~ determined by ~~measur~~ing ~~ment~~ ~~the of~~ weight loss ~~that~~
128 ~~follow~~ing ~~the~~ combustion of about 1 g of charcoal in a crucible at 950 °C. ~~With~~
129 ~~Following the same the same~~ procedure, ~~as the volatile matter,~~ the ash content was
130 determined at 750 °C. The pH of each mixture (~~pH at 1:10, (w/v) ratio~~) was measured

131 with ~~at~~the MP220 pH-meter. Micro- and meso-porosity ~~was~~were evaluated by the
132 ~~iodine~~ (I₂) and methylene blue (MB) adsorption capacity, respectively, following a
133 previously proposed ~~the~~ methodology (~~used by~~ Gaspard et al., ~~(~~2007). The specific
134 surface area was determined using N₂ sorption isotherms run on an automated surface
135 area. The specific surface~~--~~area distribution was ~~taken~~obtained from the adsorption
136 isotherms, using the ~~equation of~~ Brunauer–Emmett–Teller (BET) equation ~~surface area~~
137 (Zhang et al., 2011).

138

139 2.2.1 Elemental Composition

140 The elemental composition of ~~carbon~~ (C), ~~hydrogen~~ (H), and ~~nitrogen~~ (N) was
141 determined using an eElemental analyzer (Thermo Finnigan EA-1112, Thermo Fisher
142 Scientific Inc., Massachusetts, America); ~~and~~ the ~~oxygen~~ (O) content was determined
143 by Vario El cube, Elementar Analysensysteme GmbH Co.

144

145 2.2.2 Thermal Aalysis

146 The ~~t~~Thermal analysis of the biochars was ~~measured~~performed by using an SDT-2960
147 simultaneous DSC-TGA thermal analyzer (TA instruments) under static~~--~~air atmosphere
148 with the following temperature ramp, e.g.: ~~a~~ temperature equilibrating at 30 °C,
149 followed by a linear heating (at a rate of 5 °C min⁻¹), from 30 to 105 °C; ~~an~~ isotherm
150 for 10 min, and then continued ramping of 5 °C min⁻¹, from 105 to 680 °C.

151

152 2.2.3 Infrared Spectra

153 ~~Infrared~~ spectra were recorded on a Varian 670-IR (Agilent Technologies Inc., CA)
154 using the pellet technique by mixing 1 mg of dried biochar with 300 mg of pre-dried
155 and pulverized spectroscopic-grade KBr (from Merck & Co., Whitehouse Station, NJ).
156 The following broad~~--~~band assignationassignment was used (Chen and Chen, 2009;

157 | Haslinawati et al., 2011; Novak et al., 2010; Peng et al., 2011; Yuan et al., 2011; Wu et
158 | al., 2012; Guo and Chen, 2014): 3400 to 3410 cm^{-1} , H-bonded O–H stretching
159 | vibrations of hydroxyl groups from alcohols, phenols, and organic acids; 2850 to 2950
160 | cm^{-1} , C–H stretching of alkyl structures; 1620–1650 cm^{-1} , aromatic and olefinic C=C
161 | vibrations, C=O in amide (I), ketone, and quinone groups; 1580 to 1590 cm^{-1} , COO^-
162 | asymmetric stretching; 1460 cm^{-1} , C-H deformation of CH_3 group; 1280–1270 cm^{-1} ,
163 | O-H stretching of phenolic compounds; ~~and~~ three bands around 460 cm^{-1} , 800 cm^{-1} , ~~a₂~~
164 | ~~and~~ 1000–1100 cm^{-1} , bending of Si-O stretching.

165 |

166 | 2.2.4 Solid-state Nuclear Magnetic Resonance spectroscopy (NMR) Spectroscopy

167 | –Cross-polarization magic angle spinning (CPMAS) ^{13}C nuclear magnetic resonance
168 | (^{13}C -NMR) spectra were acquired ~~in~~ from the solid samples with a Varian 300,
169 | equipped with a 4-mm-wide bore MAS probe, operating at a ^{13}C resonating frequency
170 | of 75.47 MHz. The ~~assignment~~ assignment of the following peaks and broads was used
171 | (Brewer et al., 2009; Calvero et al., 2011). ~~The peak around 30 ppm, is was assigned to~~
172 | ~~considered as content of the~~ methylenic chains and/or CH_2 groups ~~deriving of the from~~
173 | various lipid compounds and plant waxes; ~~the t~~Two peaks at 55 ppm and 70 ppm ~~were;~~
174 | assigned to methoxy and O-alkyl groups, characteristic of ~~the~~ relatively easily ~~-~~
175 | biodegradable compounds such as ~~remaining~~ cellulose, and hemicellulose; ~~t~~The broad
176 | band around 130 ppm ~~was, assigned related~~ to alkyl substitutions in the p-hydroxy
177 | phenyl ring of the cinnamic and p-coumaric units of both lignin and suberin
178 | biopolymers, as well as to both partially degraded lignin structures and condensed
179 | aromatic and olefinic carbons; ~~t~~The sharp peak at 170 ppm ~~was,~~ assigned to the large
180 | content of carboxyl groups in the aliphatic acids of plant and microbial origin and/or
181 | amide groups in amino acid moieties. The spectra were integrated in the chemical shift
182 | (ppm) resonance intervals of 0–45 ppm (paraffinic carbons), 46–65 ppm (methoxy C

183 from OCH₃, and complex aliphatic carbons), 66–90 ppm (O-aliphatic C, such as
184 alcohols and ethers), 91–145 ppm (aromatic carbon), 145–160 ppm (phenolic carbons),
185 160–185 ppm (carboxyl, amides, and ester) and 185–220 ppm (carbonyls) (Wang et al.,
186 2007; Zhang et al., 2012).

187

188 3. Result and Discussion

189 3.1. Biochar Physicochemical Characteristics of biochar

190 The characteristics of the biochars originated derived from different agricultural wastes
191 are shown in Table 1. Low-temperature pyrolysis produced a higher biochar yield and
192 an enriched volatile-matter composition than the high-temperature biochars. The
193 biochar yields and volatile contents were gradually reduceddiminished as they
194 increasing pyrolysis temperature increaseds. Moreover, the type of feedstock also
195 affected the biochar yields and the volatile-matter content. Among the different biochar
196 types, woody biochars (AB and OB) showed a larger variation-change in the volatile
197 content from low temperature to high temperature (from 400 °C to 800 °C) than non-
198 woody biochars (RS and RH), as previously observed (by Enders et al., (2012). These-It
199 was authors found that the recalcitrant character of lignin in woody feedstocks can
200 partially resist pyrolytic decomposition at 400 °C, but not in the range of at
201 temperatures as high as 950 °C (for example, used for the determination of the ash
202 content); this leads to an, increaseing in the volatile content of the woody biochar
203 prepared at relatively low temperatures. The biochars derived from rice material (RS
204 and RH) have showed a high ash content in at all temperature ranges, whichthis may be
205 the cause for the -have easued a partial change in the structure and composition
206 promoted by a possible interaction between organic and inorganic constituents during
207 the feedstock pyrolysis, as already reported (by Elders et al., (2012), in the biochars
208 that containig an amount of ash larger than -above-20% of ashes. Rice plants are

209 ~~enriched rich within~~ Si; ~~this may be due , which strongly relates to~~ the ash content of the
210 biochar (Mukome et al., 2013), ~~which favors the by the~~ formation of ~~the~~ Si-C bonds,
211 ~~thereby which~~ increases ~~ing~~ the ~~number of~~ aromatic components and recalcitrance of the
212 biochars ~~as a result of an with~~ increase in the ~~ing~~ pyrolysis temperatures (Guo and Chen,
213 2014). In the case of woody feedstocks, recalcitrant carbons such as lignin ~~content~~ are
214 ~~the main component~~ ~~predominantly contained in woody plants~~ (Liu and Zhang, 2009;
215 Spokas et al., 2009; Joseph et al., 2013).

216 The pH values increased with temperature, probably as a consequence of the relative
217 concentration of non-~~pyrolyzed~~ ~~pyrolysed~~ inorganic elements, already present in the
218 original feedstocks (Novak et al., 2009). The porosity and surface area (~~represent~~ the
219 ~~most important main~~ physical properties of biochar), ~~which are~~ ~~critical factors for~~
220 ~~strongly connected with~~ the improvement of soil properties such as soil adsorption
221 capacity and water retention ability ~~ies~~ (Kalderis et al., 2008). The application of ~~the RH~~
222 biochar ~~derived from the rice husk~~ has been reported to enhance these properties ~~in the~~
223 ~~soil~~ (Kalderis et al., 2008; Liu and Zhang, 2009; Lei and Zhang, 2013). As shown in
224 Table 1, ~~the a~~ biochar production at higher temperatures generally ~~enlarged~~ ~~leads to an~~
225 ~~increase in the MB~~ ~~methylene blue~~ number, I₂ absorption, and surface area, compared to
226 the production at lower temperatures (p < .001); ~~this is in line , and these results are in~~
227 ~~accordance~~ with ~~other~~ previous ~~studies~~ ~~work~~ (Gaskin et al., 2008; Liu and Zhang, 2009;
228 Yu et al., 2011). ~~In addition, Regarding of comparison among the variety of origins, our~~
229 ~~data showed that~~ the difference ~~in in the~~ micro-porosity (I₂) ~~of between the~~ biochars
230 ~~obtained between~~ from wood feedstock (AB and OB) and ~~those~~ from rice residues (RH
231 and RK) ~~was~~ gradually ~~enlarged~~ ~~increased~~ as ~~the increasing~~ pyrolysis temperature ~~from~~
232 ~~increased from~~ 500 °C to 800 °C. ~~In addition, In contrast, an apparent difference in~~
233 ~~surface area was observed. t~~ The surface areas of RH and RK ~~reduced~~ ~~diminished~~ at
234 800 °C, while those of AB and OB ~~still had been~~ ~~expanded~~ ~~tending~~. The ~~former~~

235 ~~behavior se decreases in surface area~~ ~~was s~~ of RH and RK will be attributed to the ash
236 content in the biochar, which, ~~that high content of inorganic ash in biochar~~ filled or
237 blocked the access to micropores, resulting in a relatively low surface area (Mackay and
238 Roberts, 1982; Song and Guo, 2012).

239 240 3.2. Analytic Elements

241 Analytical elements and both ~~ratios of~~ H/C and O/C ~~ratios~~ are also useful indicators
242 ~~of to evaluate~~ the characters of biochars (Nguyen and Lehmann, 2009). ~~As Data in~~
243 ~~shown Table 2 suggest that~~, ~~it is observed that~~ an increase in the ~~the increasing~~
244 temperature results in a larger loss of hydrogen-H and oxygen-O compared to that of
245 ~~than carbon C~~. ~~The d~~Dehydrogenation of CH₃ (~~on biochar properties as consequence a~~
246 result of thermal induction) indicates is the indicative of a changes in the biochar
247 recalcitrance (Harvey et al., 2012). ~~Concerned with oxy~~In addition ~~oxygen loss~~, ~~the a~~
248 biomass material normally typically comprises ~~of~~ labile and recalcitrant O fractions; the
249 former a labile O fraction that is rapidly quickly lost upon after the initial heating, the
250 latter and a recalcitrant O fraction which is retained in the char of the final product
251 (Rutherford et al., 2013).

252 Because of the high temperature of the charring process, ~~Regarding with t~~the H/C/
253 and O/C ratios (~~Table 2~~) are ~~shows the reduced~~, as a result ~~tion in these ratios with~~
254 charring temperature, being attributed to ~~of~~ the dehydration and decarboxylation
255 reactions. ~~The change of~~ The O/C ratio in the range from 400 °C to 500 °C range was
256 remarkably changed according to the following observed in the order: ~~of~~ RS > RK > AB
257 > OB. Yang et al., (2007) and Khodadad et al., (2011) found that the biochar made
258 derived from wood ~~and~~ at higher temperatures is are less biologically labile, because it
259 contains a containing relatively higher larger proportions amount of ~~more~~ aromatic-
260 organic matter; ~~compared to~~ that of other biochars prepared from agricultural residues

261 ~~and~~ at lower temperatures. As shown in the van Krevelen diagram (Fig. 1), ~~the~~
262 ~~constancy of the reduction in~~ the H/C and O/C ratios ~~steadily diminish~~ as ~~the~~
263 ~~temperature increases, increasing temperature are observed,~~ reflecting the loss of easily
264 degradable carbon compounds such as volatile matters. ~~At the parallel~~ Similarly, a lower
265 C/O ratio ~~in biochar with~~ higher temperatures ~~indicate~~ indicates ~~the an~~ arrangement of
266 ~~the~~ aromatic rings (Spokas et al., 2010), ~~which~~ forming ~~very stable~~ crystal graphite-like
267 structures ~~with high stability~~ (Wu et al., 2012; Dong et al., 2013).

268 ~~Concerning A comparison of the with the difference of the~~ feedstocks in the
269 diagram ~~indicates that,~~ the ~~rice materia~~ RS and RH biochars (~~RS and RH~~) ~~were are~~
270 distanced from ~~the~~ Y axis at $600\text{ }^{\circ}\text{C}$ and $700\text{ }^{\circ}\text{C}$; whereas ~~the H/C and O/C ratios in~~
271 ~~the AB and OB biochars show at~~ the stable reduction ~~of the H/C and O/C in wood~~
272 ~~biochars (AB and OB) was shown.~~ The reduction of ~~the~~ carbon content in ~~the~~ biochar
273 production ~~could may~~ be related to the chemical and physical composition. ~~In particular,~~
274 ~~a previously proposed SEM-EDS analysis suggested a~~ The change ~~of in~~ the physical and
275 structural composition of ~~the rice straw~~ RS biochar ~~obtained at between t~~ the pyrolysis
276 ~~temperatures of e~~ condition of $500\text{ }^{\circ}\text{C}$ and $700\text{ }^{\circ}\text{C}$ is reported by Guo and Chen (2014),
277 ~~using SEM-EDS images~~ (Guo and Chen, 2014). For the rice husk biochar made at 500
278 $^{\circ}\text{C}$, ~~In addition,~~ the silicon of the RH biochar obtained at $500\text{ }^{\circ}\text{C}$ was associated with
279 ~~the formation of a carbon and formed a dense carbon~~ structure, ~~(forming Si-~~
280 ~~encapsulated carbon); in contrast, , meanwhile the silicon component were physically~~
281 ~~distanced from carbon structure in the~~ biochars prepared at the highest temperature (700
282 $^{\circ}\text{C}$), ~~the silicon component was physically distanced from the carbon structure.~~

283

284 3.3. Thermal ~~A~~ analysis

285 Thermal analysis is a useful method to ~~understand study~~ the structure of biochar
286 materials (Kalderis et al., 2014; Mimmo et al., 2014). In ~~our this work, study~~ (Fig. 2),

287 all biochar samples ~~had showed~~ a similar thermal degradation profile (Fig. 2), with ~~an~~
288 ~~the increasing~~ weight loss ~~proportionally increasing~~ with ~~increasing~~ ~~pyrolysis~~
289 ~~temperature of pyrolysis~~. ~~In this respect, a clear~~ The difference among the feedstocks
290 (wood vs. non-wood) was observed ~~in the total weight losses, as observed in the ash~~
291 ~~content, i.e.,~~ ~~The curves of the lost~~ weight ~~loss in of~~ AB and OB, ~~and RH and RK~~
292 ~~reached was up to 90% and 40–50% percent of the~~ total weight, ~~respectively~~;
293 ~~meanwhile this behavior~~ ~~the curve in RH and RK reached around half volume of~~
294 ~~weight (40–50%), reflecting~~ the higher mineral content in rice materials. ~~In addition,~~
295 ~~and moreover during charring process~~ this mineral ~~component content performs~~
296 ~~functions~~ as a barrier ~~that~~ prevents ~~from the diffusion of~~ heat ~~diffusion~~ and therefore
297 ~~the~~ release of the volatile ~~component~~ ~~tents~~ ~~during the charring process~~ (Xu and Chen,
298 2013).

299

300 3.4. Chemical ~~C~~omposition with ~~S~~pectra ~~P~~arameters (FT-IR and NMR)

301 ~~The FT-IR is a great tool to observe the shift change of chemical composition. The~~
302 ~~aliphatic loss process is represented by~~ ~~The~~ FT-IR band at $2950\text{--}2850\text{ cm}^{-1}$ (which
303 ~~appears in the temperature range of 400 and 600 °C) was assigned to the~~ ~~of FT-IR with~~
304 ~~aliphatic C-H stretching~~ ($2950\text{--}2850\text{ cm}^{-1}$) ~~at increasing temperature from 400 °C to~~
305 600 °C (Figure 2); ~~this indicates an aliphatic loss~~. ~~In addition, meanwhile~~ the
306 ~~typical representative~~ peaks ~~of for~~ aromatic carbon ~~appeared more clearly~~; these were
307 ~~appeared more clearly~~ ~~assigned to the~~ such as C-H stretching ($750\text{--}900\text{ cm}^{-1}$) ~~a~~ and
308 $3050\text{--}3000\text{ cm}^{-1}$, C=C ($1380\text{--}1450\text{ cm}^{-1}$), C-C and C-O stretching ($1580\text{--}1700\text{ cm}^{-1}$).
309 ~~These data suggest that~~ ~~As shown by the infrared spectra,~~ the charring temperature ~~can~~
310 ~~modify~~ the functional groups, ~~leading to a decrease in,~~ ~~the~~ ~~and thus~~ aliphatic C
311 groups ~~and decrease an increase in~~ but aromatic C ~~increases~~ (Lee et al., 2010). Since ~~the~~
312 ~~biochar~~ longevity ~~of biochar is a matter of debate~~ in relation with ~~the~~ ~~its~~ biochar

313 production is still a matter of debate (Nguyen and Lehman, 2009; Peng et al., 2011), the
314 pyrolysis process ~~of at~~ 600 °C, which ~~creates~~ leads to a higher ~~more~~ recalcitrant
315 character by increasing the number of aromatic compounds, ~~has is a~~ suitable method ~~in~~
316 ~~for terms of the~~ carbon sequestration. However, when the charring temperature
317 increases to values larger than ~~over~~ 700 °C ~~and~~ 800 °C, the intensity of the bands such
318 as that of ~~decline gradually such as the~~ hydroxyl groups (3200–3400 cm⁻¹) and ~~even~~
319 aromatic ~~bands~~ groups (1580–1600 cm⁻¹ and 3050–3000 cm⁻¹) gradually diminishes.
320 ~~Other Previous studies works~~ (Yuan et al., 2011) have shown that ~~report that~~ the
321 number of bands representing functional groups are present ~~at in~~ biochars obtained at
322 ~~the lower~~ temperature biochars (300 °C and 500 °C), and are absent in those derived e
323 ~~biochar derived by at~~ 700 °C.
324 In particular, ~~The characteristic of feedstock type of biochar has been reflected by~~ ~~t~~he
325 presence of ~~b~~ bands around 460 cm⁻¹, 800 cm⁻¹, and 1040–1100 cm⁻¹, which were
326 assigned to SiO₂, reflects the nature of the feedstock type; ~~and~~ these bands ~~was were~~
327 observed in ~~shown in all the~~ RH and RS biochars ~~originated from rice materials (RH~~
328 ~~and RS), showing in the~~ (Fig. 3–b). In plant physiology, ~~the presence of~~ silica is
329 knowingly known to be found ~~as the most critical~~ ~~principle~~ component ~~of for~~ plant
330 phytoliths, ~~as~~ phytoliths ~~and it it functions for~~ ~~protection the of the~~ plant carbon from
331 degradation (Wilding et al., 1969; Parr, 2006). ~~In deed~~ fact, SiO₂ is a major component
332 in the chemical structure of rice material. ~~The shoulder observed around 1600 cm⁻¹ in~~
333 ~~rice the~~ RH and RS biochars ~~(RH and RS), which was~~ assigned to the aromatic
334 compounds, is still present ~~retained~~ at temperatures as high as ~~until the~~ 800 °C during
335 the biochar production. Guo and Chen (2014) proposed ~~that a novel framework of novel~~
336 silicon- ~~and~~ carbon framework that ~~couple may provide can contribute~~ a new
337 perspective for the evaluation of ~~ng~~ the biochar stability, in addition to ~~the~~ besides
338 recalcitrant character derived from the aromatic carbon compounds. In particular, ~~They~~

339 ~~mention that~~ the structure of encapsulated carbon by silica ~~could~~ can protect the biochar
340 against physical and chemical oxidation, ~~and~~ presumably leadings to a longer turnover
341 time in soils.

342 The ^{13}C NMR spectra of different biochars ~~(are shown in Fig. 3 (a and b))~~ with
343 similar show shape for all biochar materials a strong dominated by the presence of
344 condensed aromatic signal at 127 ppm. ~~Furthermore, this signal~~ signal was becomes
345 more intense in the observed more clearly in all different biochars ~~which are~~ produced
346 at 600 $^{\circ}\text{C}$; however, ~~and the sharpness of this peak was gradually weaken~~ as the
347 temperature increases ~~and~~ (above 600 $^{\circ}\text{C}$), this peak loses sharpness. ~~Same trend was~~
348 ~~shown in~~ The shoulder of the methoxyl carbons of lignin and that of carboxylic carbons,
349 at 57 ppm and 190 ppm, respectively, shows a similar trend, i.e., ~~Especially, the~~
350 ~~biochars, made from rice straw at 800 $^{\circ}\text{C}$ (Fig. 3, b) demonstrated a~~ the decomposition
351 of this shoulder was observed for the RS biochars obtained at 800 $^{\circ}\text{C}$ (Fig. 3b). ~~of these~~
352 ~~ranges. From~~ Thus, these results along with those of the is result as well as shown in FT-
353 IR analysis suggest figure, it worth of noting that there is ~~that s~~ no much need to produce
354 biochara ~~with very high temperature (700–800 $^{\circ}\text{C}$ and 800 $^{\circ}\text{C}$)~~ may affect for
355 preserving the chemical properties of the functional groups and the stability echaracter of
356 the biochars, as a result of based on the predominance the formation of aromatic
357 structures and keeping higher chemical property with functional groups.

358 ~~Concerning with lower temperature,~~ The shoulder observed at around 20 ppm,
359 which was assigned to easily degradable carbon compounds, appeared ~~in~~ for the
360 biochars produced at 400 $^{\circ}\text{C}$ produced biochars; ~~and~~ this shoulder was not detected
361 eliminated in the biochar~~s~~ produced at 500 $^{\circ}\text{C}$. This ~~accords~~ is in agreement with
362 previous studies other's work (McBeath et al., 2013) that have shown that the biochar~~s~~;
363 produced at temperatures of 300 $^{\circ}\text{C}$ –400 $^{\circ}\text{C}$, exhibited ~~ed~~ broad alkyl signals and
364 carbohydrate bands; ~~meanwhile~~ these bands were not detected ~~able above~~ over 400 $^{\circ}\text{C}$.

365 As shown in the previous section, the biochar~~s~~, produced at lower temperatures, contain
366 a large amount of ~~has higher~~ volatile carbon ~~contents~~. Thise type of easily degradable
367 compounds possibly contributes to microorganisms in soil as substrate (Khodadad et al.,
368 2011). ~~In this sense~~ Thus, a lower temperature may be more~~is~~ suitable for the application
369 of the ~~for the~~ biochar~~s~~ for the improvement of ~~utilization for~~ soil fertility. ~~On the~~
370 ~~contrary~~ In contrast, higher ~~temperature~~ pyrolysis selects functional groups and
371 provides aromatic predominant presence in chemical composition, consequently
372 resulting to the formation of recalcitrant structure. ~~However,~~ it should be remarked
373 that should be highlighted that the excess of the high temperatures as high as such as
374 700 ~~°C~~ and ~~800~~ °C are ~~not~~ likely suitable for ~~and~~ an efficient biochar
375 production, ~~for biochar~~ i.e., the heat degradation of the functional groups ~~production,~~
376 ~~since th~~ may reduce the ~~ose biochars reduce~~ recalcitrant character, thus resulting in a ~~by~~
377 ~~heat degradation of functional group, and lower biochar yield~~ lower the biochar
378 production than other biochars.

379

380 4. Conclusion

381 The data presented in this work clearly showed that both ~~In conclusion, the~~ the
382 pyrolysis temperature ~~of pyrolysis~~ and the type of feedstock drive the physico-chemical
383 properties of the biochar~~s~~. ~~In our particular, an study,~~ increase ing r in the temperature
384 improved the ~~enhanced the physical property of~~ adsorption properties~~y~~ such as large
385 surface area, and porosity, and the recalcitrant chemical character in woody ~~material~~
386 biochar~~s~~ (AB and OB). ~~In~~ By contrast, rice ~~material~~ biochar (RH and RS) ~~has~~ shows a
387 higher biochar yield during the pyrolysis process than that of AB and OB. In addition,
388 ~~and the propertiesy~~ of the rice-material biochar products are~~is~~ different from woody
389 ~~material~~ biochars, i.e., ~~in that~~ the inorganic components are~~is~~ combined with organic
390 moieties as a consequence of the ~~in related with the~~ carbon encapsulation promoted

391 | ~~by~~ silicon ~~presence~~. Finally, ~~t~~The over-heat production (temperature above 600 °
392 | °C) ~~showed~~ causes the decomposition ~~disappearance~~ of the functional groups through,
393 | ~~driven by~~ heat degradation.

394

395 | **5.Acknowledgements**

396 | This work was partly supported ~~in part~~ by the JSPS-CSIC bilateral project.

397

Table 1. Physical and chemical characteristics of the biochars derived from different feedstocks; AB (apple tree branch), OB (oak tree), RH (rice husk), and RS (rice straw).

samples	temperature (°C)	Biochar Yield (%)	Ash Content (%)	Volatile Content (%)	pH (H ₂ O)	Methylene Blue (mg/g DW)	I ₂ adsorption (mg/g DW)	BET Surface Area (m ² /g)
AB	400	28.3	4.4 ± 0.0	32.4 ± 0.1	7.02 ± 0.08	4.4 ± 0.2	45.0 ± 2.6	11.9
	500	16.7	6.5 ± 0.0	18.3 ± 0.3	9.64 ± 0.07	2.0 ± 0.4	97.9 ± 2.7	58.6
	600	16.6	7.6 ± 0.1	11.1 ± 0.2	10.04 ± 0.02	5.7 ± 0.4	122.1 ± 1.5	208.7
	700	15.8	8.0 ± 0.0	7.7 ± 0.1	10.03 ± 0.02	0.6 ± 0.7	208.3 ± 1.5	418.7
	800	15.5	8.6 ± 0.0	6.8 ± 0.1	10.02 ± 0.02	1.8 ± 0.6	298.5 ± 1.7	545.4
OB	400	35.8	3.6 ± 0.0	32.1 ± 0.1	6.43 ± 0.04	3.9 ± 0.3	38.7 ± 0.0	5.6
	500	28.6	5.1 ± 0.1	19.4 ± 0.3	8.10 ± 0.12	5.6 ± 0.5	91.7 ± 0.1	103.2
	600	22.0	5.54 ± 0.0	12.3 ± 0.0	8.85 ± 0.07	5.5 ± 0.4	131.3 ± 1.5	288.6
	700	20.0	6.2 ± 0.0	8.3 ± 0.1	9.54 ± 0.00	7.1 ± 0.2	212.8 ± 0.1	335.6
	800	19.1	8.3 ± 0.2	7.9 ± 0.1	9.68 ± 0.03	9.4 ± 0.5	250.3 ± 1.4	398.2
RH	400	48.6	35.9 ± 0.1	22.0 ± 0.1	6.84 ± 0.03	2.9 ± 0.8	44.1 ± 1.6	193.7
	500	42.4	46.2 ± 0.2	10.6 ± 0.1	8.99 ± 0.04	9.7 ± 0.4	75.4 ± 1.6	262.0
	600	37.3	52.8 ± 0.4	6.0 ± 0.3	9.41 ± 0.00	3.5 ± 0.2	69.0 ± 3.1	243.0
	700	32.8	55.1 ± 0.2	3.9 ± 0.1	9.52 ± 0.02	3.9 ± 1.0	121.0 ± 1.6	256.0
	800	32.0	62.6 ± 0.3	3.2 ± 0.2	9.62 ± 0.01	4.1 ± 0.3	174.4 ± 3.1	295.6
RS	400	39.3	34.0 ± 0.2	22.4 ± 0.1	8.62 ± 0.03	9.3 ± 2.4	74.7 ± 2.6	46.6
	500	32.6	43.5 ± 0.2	12.8 ± 0.1	9.82 ± 0.01	9.6 ± 2.8	95.9 ± 1.5	59.9
	600	23.4	58.6 ± 0.1	8.4 ± 0.0	10.19 ± 0.01	3.7 ± 4.9	85.6 ± 1.6	129.0
	700	18.4	69.9 ± 0.4	5.3 ± 0.1	10.39 ± 0.03	0.5 ± 3.0	100.6 ± 1.5	149.0
	800	18.3	73.9 ± 0.1	4.5 ± 0.2	10.47 ± 0.04	2.6 ± 2.0	190.2 ± 1.3	256.97

Table 2. The elemental compositions of the -biochars derived from different feedstocks; AB (apple tree branch), OB (oak tree), RH (rice husk), and RS (rice straw).

samples	temperature (°C)	C* (%)	H* (%)	N* (%)	O (%)	O/C	H/C
AB	400	70.2 ± 0.2	4.13 ± 0.01	0.76 ± 0.00	20.6± 0.1	0.22	0.71
	500	79.1 ± 0.0	2.65 ± 0.09	0.34 ± 0.01	12.0± 0.1	0.11	0.40
	600	81.5 ± 0.1	1.96 ± 0.02	0.46 ± 0.00	13.6± 0.3	0.12	0.29
	700	82.3 ± 1.4	1.21 ± 0.05	0.41 ± 0.02	16.3± 0.7	0.15	0.18
	800	84.8 ± 0.1	0.60 ± 0.01	0.34 ± 0.01	5.8±0.0	0.05	0.08
OB	400	70.5 ± 0.2	3.70 ± 0.02	0.69 ± 0.02	21.5± 0.2	0.23	0.63
	500	77.6 ± 0.3	2.51 ± 0.16	0.51 ± 0.03	17.7± 0.5	0.17	0.39
	600	81.2 ± 0.5	1.92 ± 0.01	0.48 ± 0.02	16.0± 0.2	0.15	0.28
	700	83.2 ± 0.2	1.16 ± 0.06	0.31 ± 0.00	15.0± 0.1	0.13	0.17
	800	82.9 ± 0.4	0.69 ± 0.06	0.32 ± 0.00	17.3± 0.1	0.16	0.10
RH	400	44.6 ± 0.3	2.50 ± 0.00	0.69 ± 0.02	16.3± 0.2	0.27	0.67
	500	45.2 ± 0.3	1.27 ± 0.03	0.47 ± 0.02	7.1± 0.2	0.12	0.34
	600	40.4 ± 0.7	0.85 ± 0.05	0.37 ± 0.01	9.2± 0.3	0.17	0.25
	700	38.8 ± 0.5	0.46 ± 0.04	0.26 ± 0.02	12.7± 0.2	0.25	0.14
	800	40.4 ± 0.7	0.28 ± 0.01	0.22 ± 0.00	2.7± 0.0	0.05	0.08
RS	400	49.9 ± 0.2	2.80 ± 0.12	1.22 ± 0.01	12.0± 0.1	0.18	0.67
	500	37.5 ± 0.2	0.93 ± 0.03	0.61 ± 0.01	8.6± 0.3	0.17	0.30
	600	33.8 ± 1.0	0.60 ± 0.07	0.41 ± 0.04	13.7± 0.3	0.30	0.21
	700	36.3 ± 0.8	0.51 ± 0.06	0.34 ± 0.02	17.4± 0.9	0.36	0.17
	800	29.2 ± 0.4	0.25 ± 0.02	0.25 ± 0.01	3.7± 0.0	0.10	0.10

Figure legends

Fig. 1.- Van Krevelen diagram of the biochars derived originated from different feedstocks; AB (apple tree branch), OB (oak tree), RH (rice husk), and RS (rice straw). Each symbol shows-indicates the pyrolysis temperature -as follows: Black = 8000_C, Gray = 7000_C, Line = 6000_C, Dot = 5000_C, and White = 4000_C.

Fig. 2. a.—Thermal analysis of the biochars obtained from (a) of wood materials; (AB (apple tree) and OB (oak tree)) and (b)

Fig. 2. b.—Thermal analysis of biochars of of rice residues (RH (rice husk-) and RS (rice straw)).

Fig. 3. a.— FT-IR spectra of the biochars obtained from (a) of wood materials (AB (apple tree) and OB (oak)) and (b). Fig. 3. b.— FT-IR spectra of biochars of rice residues (RH (rice husk) and RS (rice straw)).

Fig. 4. ¹³C a.— ¹³C CPMAS-NMR of the biochars obtained from (a) of wood materials (AB (apple tree) and OB (oak tree)) and (b)

Fig. 4. b.— ¹³C CPMAS NMR of biochars of rice residues (RH (rice husk) and RS (rice straw)).

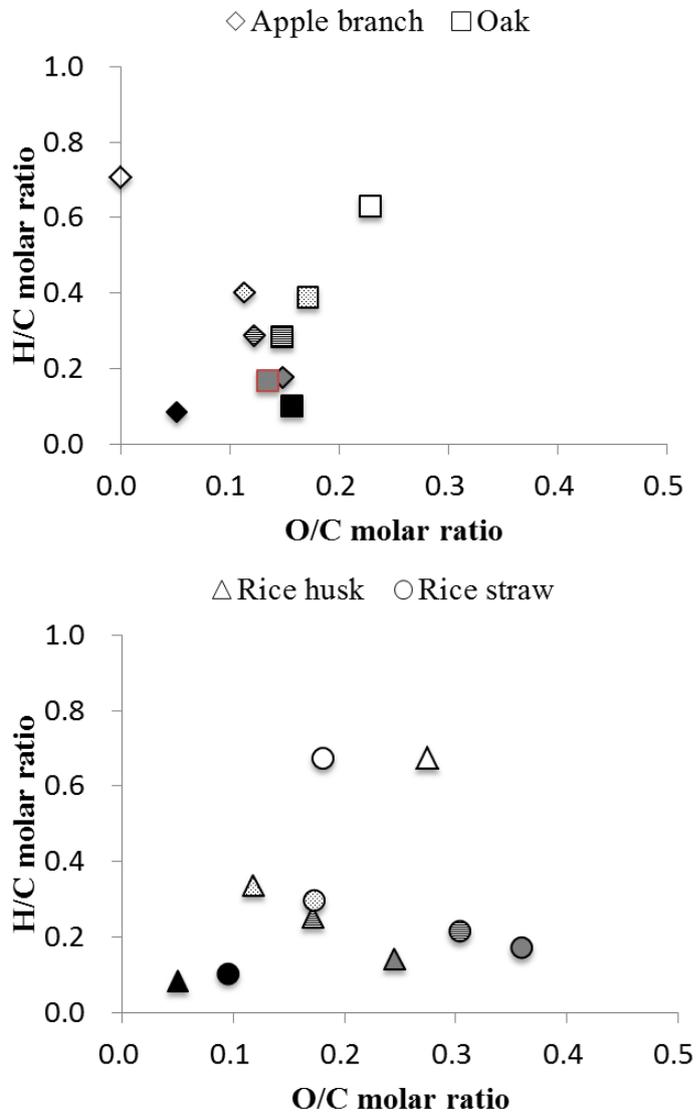


Fig. 1 Van Krevelen diagram of biochar originated from different feedstock.- The temperature range of pyrolysis process is as following; Black = 800°C; Gray = 700°C; Line = 600°C; Dot = 500°C; and White = 400°C

書式変更: 上付き/下付き(なし)

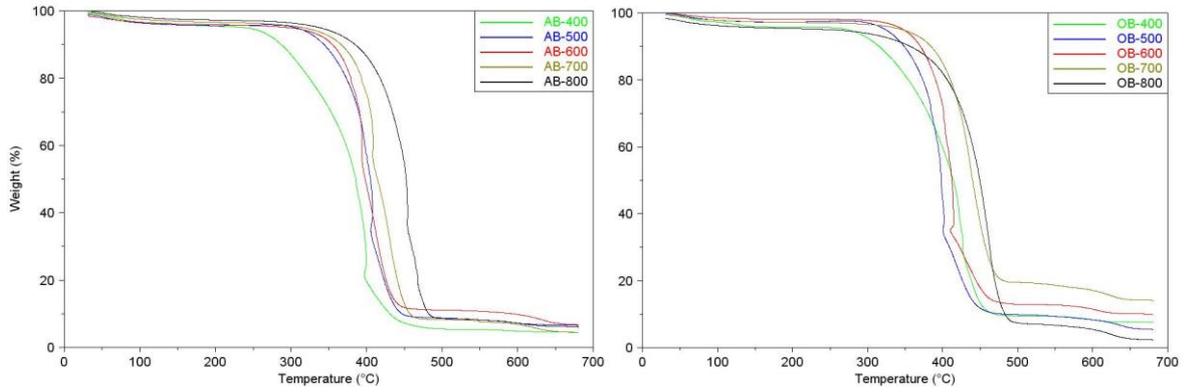


Fig. 2. a. - Thermal analysis of biochars of wood materials; AB (apple tree) and OB (oak tree)

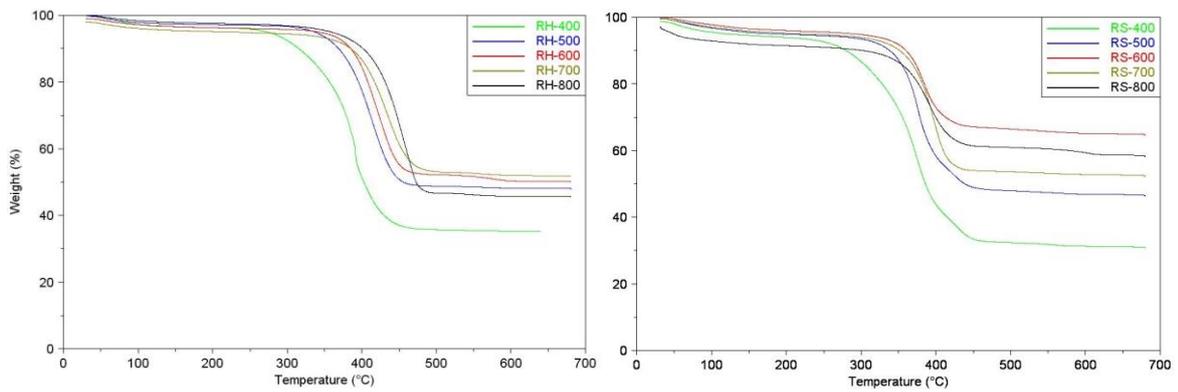


Fig. 2. b. - Thermal analysis of biochars of rice residues; RH (rice husk) and RS (rice straw)

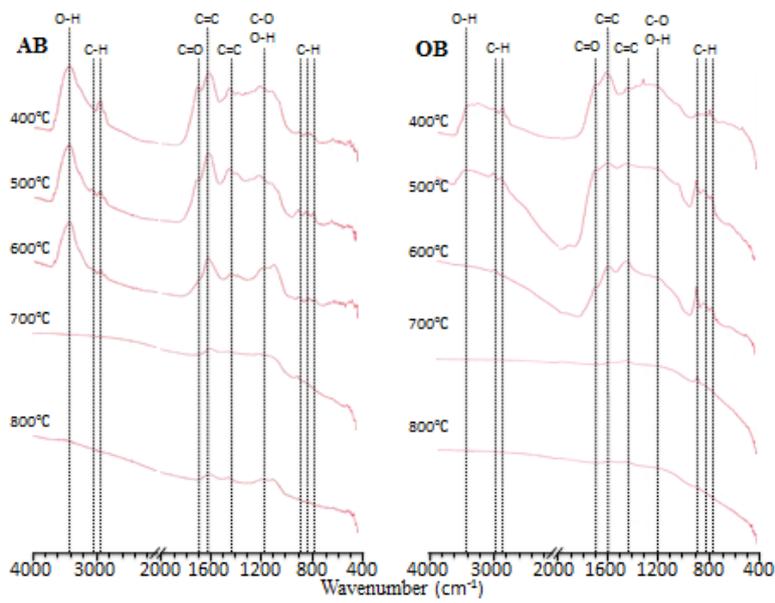


Fig. 3.a.-FT-IR spectra of biochars of wood materials; AB (apple tree) and OB (oak tree)

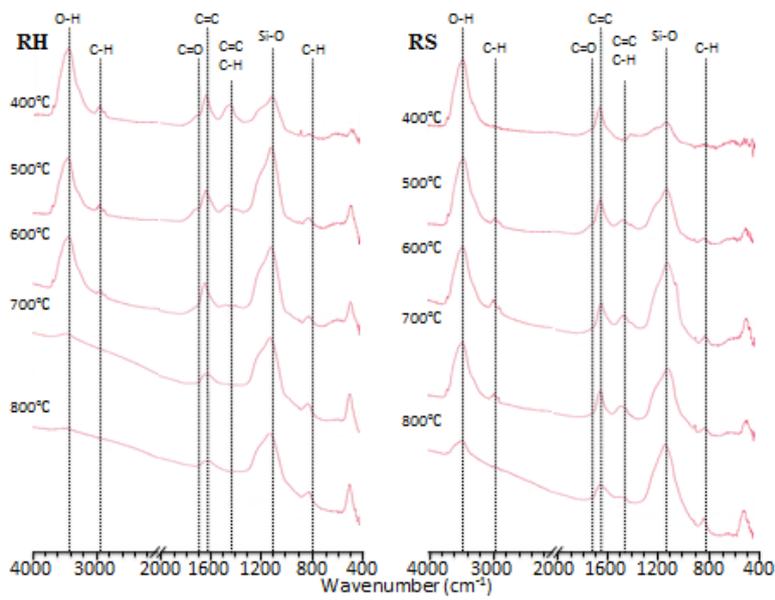


Fig. 3.b.-FT-IR spectra of biochars of rice residues; RH (rice husk) and RS (rice straw)

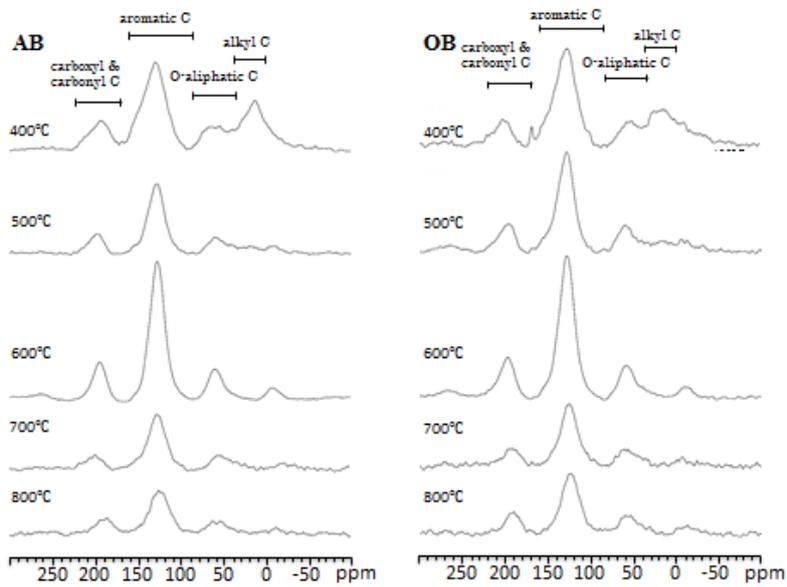


Fig. 4. a. ^{13}C CPMAS-NMR of biochars of wood materials; AB (apple tree) and OB (oak tree)

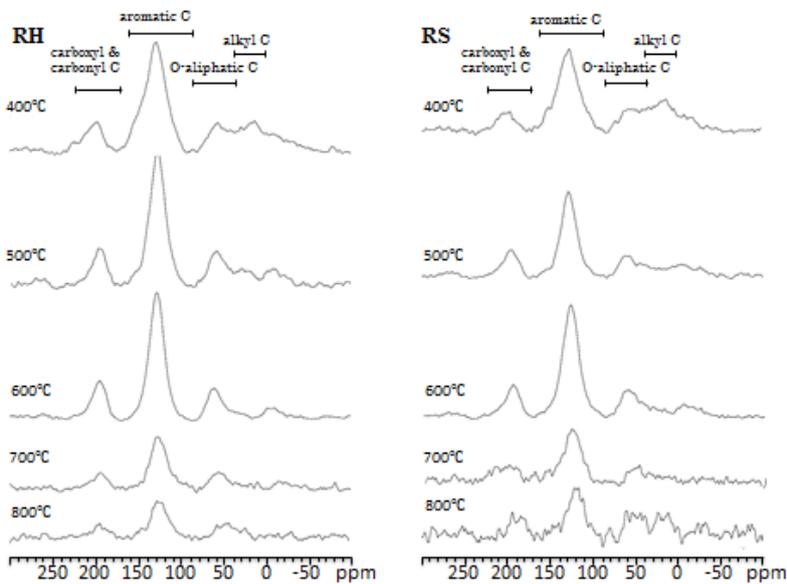


Fig. 4. b. ^{13}C CPMAS-NMR of biochars of rice residues; RH (rice husk) and RS (rice straw)