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”.

As substitute for what?
Physical and Chemical Characterizations of biochars derived from different 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 identify the most suitable use in adequately application to soil (Manvi, 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 pyrolyzed 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 study. In 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, the P-pyrolysis at lower temperatures produced high had more biochar yields, but in relative to the 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
carbon content in the biochars also increased together with increased temperatures.

Infrared-Fourier spectra (FT-IR) and $^{13}$C-NMR were used to understand carbon chemical compositions in our biochars, and it was observed that the numbers of the shoulders representing aromatic groups, considered as stable carbon structure appeared as the temperature came closer to 600°C, as well as in FT-IR. In rice materials (RS and RH), the peaks assigned to SiO$_2$ was observed in different temperature ranges of biochars (400-800°C) in FT-IR along with retained small shoulder of aromatic carbon (over 1620 cm$^{-1}$). The biochar obtained from rice materials (RH and RS) has high biochar yield and the unique chemical property as a consequence of the incorporation of silica element into chemical structure, while in the biochar from wood materials (AB and OB) the enrichment with carbon content together with high absorption character was created. We propose that the pyrolysis at 600°C creates the most recalcitrant character for carbon sequestration, meanwhile the pyrolysis at 400°C produces the superior properties as a fertilizer by retaining volatile and easily labile compounds, which promotes soil microbial activities.

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

The interest in biochar utilization as a strategy for mitigation of global warming is steadily increasing. Besides the growing attention to the biochar utilization for carbon sequestration, a number of works are reported on alternative uses of biochar, such as the improvements of soil fertility, plant growth and decontamination of pollutants such as pesticides, heavy metals, and hydrocarbons (Beesley et al., 2011; Cabrera et al., 2011). Since the diverse applications of biochar would be determined by its physicochemical properties, which are governed by the pyrolysis conditions (heating temperature and duration) and the original feedstock (Enders et al., 2012). For this reason, should be in accordance with the adequate ability and property each biochar has, the information on the whole production process, which mostly determine fundamental biochar character, is a key factor in defining any strategy for the use of biochar, to understand them. Moreover, Pyrolysis is the thermo-chemical process of heating biomass under low oxygen presence to produce pyrogenic material. Heating duration, temperatures, and types of feedstock materials are main components to determine the property of final product. Pyrolysis is the thermo-chemical process of heating biomass under low oxygen presence to produce pyrogenic material. Heating condition, and types of feedstock materials are main components to determine the property of final product (Enders et al., 2012), and the differences in stability between biochars and the transformation after adding to the soil is affected by the initial property (Joseph et al., 2010). The physicochemical properties of biochar can drive changes in soil nutrient and C availability and provide physical protection of microorganisms from predators and desiccation, which finally promotes the alteration of the microbial diversity and the taxonomy (Leehman et al., 2011). Biochar derived from relatively low temperature
pyrolysis are characterized by a high content of volatile matter, containing easily decomposable substrates, which can contribute to the plant growth as an additional nutrition, according to the reports (Robarton et al., 2012; Mukherjee and Zimmerman, 2013; Lammirato et al., 2014). On the other hand, the structure of the biochar derived from the high temperature pyrolysis is was refined to more selected compounds, formed characterized by larger surface area and also showed higher aromatic carbon contents, which can could promote and finally this physico-chemical property promotes the adsorption capacity for bioremediation as well as the recalcitrant character for carbon sequestration (Lehmann, 2007). Also, it has been considered that the yields by-products such as fuels and gases generated during the pyrolysis were influenced by pyrolysis temperature and duration (Grierson et al., 2009; Mahinpey et al., 2009; Gell et al., 2011).

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

The aim of our study is to optimize the physicochemical characteristics of biochar for its use in agriculture by combining different pyrolysis conditions and the selection of different agricultural wastes as feedstocks biochar production of each different material. To achieve this aim, evaluating the thermo-chemical properties of biochars obtained derived by different feedstock with at different temperature (400-800 °C) were evaluated. Rice husk (RH) and rice straw (RS) are used in our work as original materials, since the global amounts of residues from rice crop (Oryza sativa L.) are 0.9
Gt for a year which constitutes the 25% of the total amount of whole agricultural residues in the world (Knoblauch et al, 2011). Also, the research on characteristic of biochars derived from orchard residues, pruning woodchips of apple tree (AB) (*Malus pumila*), are taking place, comparing with hard-wood biochars as well as the other tree wood chip from oak tree (OB), (*Quercus serrata*). According to the FAO statistics, the 793,800 metric tons of apple is produced in Japan in 2012, and 50 percent of the whole production are from Aomori prefecture, which is well known as the origin of variety “Fuji Apple”. However, 36,879 ton/year (dry weight) of pruning branches in this region, which estimate more than 75% of total volume, still remains without utilization (NADO report). This is probably due to the concern that the remnant of pesticide, insecticide or fire retardant, that impregnated into the wood and finally making them psychical inseparable (Badger, 2002), is hazardous material for soil ecosystem if plowing residual orchard materials as organic amendment. The carbonization of pruning woodchip could be alternative waste management not only for reducing hazardous material such as pesticide remnant (Suri and Horio, 2010) but also for sequestrating carbon in soil. Although several works on the use of pruned-biochar as soil amendment have been recently published recently for soil amendment (Fellet et al., 2011; Alburquerque et al., 2013), the evaluation of the pyrolysis during production process on this feedstock is hardly reported. The optimization of pyrolysis production should be examined by monitoring the production process.

### 2. MATERIALS AND METHODS

2.1 Biochar preparation from agricultural residues

Biochars used in this work were made from two rice residues (*Oryza sativa* L.): straw and husk, and two woody materials: a kind of broad-leaved trees (*Quercus serrate* Murray) and apple wood chips (*Malus pumila*). All materials were first dried in air and
then cut into small pieces (less than 4-5 cm) to put into a ceramic vessel (370 cm$^3$) for a commercial electric furnace (SOMO-01 Isuzu, Japan), and were charred for 10 hours at different temperatures (from 400 to 800°C) with 10 °C min$^{-1}$ heating rate.

2.2 Chemical analysis of biochar

After the pyrolysis process, all samples were grounded to be homogenized and sieved to less than 0.5 mm in diameter. The biochar yield was calculated by the proportion of the weight of pyrolysis product to the original material. The determination analysis of volatile matter and ash content was conducted according to the American Society for Testing and Materials (ASTM) D1752-84, which is recommended in the International Biochar Initiative (www.biochar-international.org). The volatile matter was determined by measurement of weight loss following combustion of about 1 g of charcoal in a crucible at 950 °C. With the same procedure as the volatile matter, the ash content was determined at 750 °C. The pH of each mixture pH at 1:10 (w/v) ratio was measured with a MP220 pH-meter. Micro- and meso-porosity was evaluated by the iodine (I$_2$) and methylene blue (MB) adsorption capacity, respectively, following the methodology used by Gaspard et al., (2007). The specific surface area was determined using N$_2$ sorption isotherms run on automated surface area. The specific surface area distribution was taken from adsorption isotherms, using the equation of Brunauer–Emmett–Teller (BET) surface area (Zhang et al., 2011).

Elemental composition

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

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

**Infrared Spectra**

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

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

**Solid-state nuclear resonance spectroscopy (NMR)**

Cross-polarisation magic angle spinning (CPMAS) ¹³C nuclear magnetic resonance (¹³C-NMR) spectra were acquired in the solid samples with a Varian 300, equipped with a 4-mm-wide bore MAS probe, operating at a ¹³C resonating frequency of 75.47 MHz. The assignation of the following peaks and broads was used (Brewer et al., 2009; Calvero et al., 2011): The peak around 30 ppm, is considered as content of methylenic chains and/or CH₂ groups deriving from various lipid compounds and plant waxes; and plant biopolyester. Two peaks at 55 ppm and 70 ppm, assigned to methoxy and O-alkyl
groups characteristic of the relatively-easily-biodegradable compounds such as remaining cellulose, and hemicellulose; The broad band around 130 ppm, related to alkyl substitutions in the p-hydroxy phenyl ring of cinnamic and p-coumaric units of both lignin and suberin biopolymers, as well as to both partially-degraded lignin structures and condensed aromatic and olefinic carbons; The sharp peak at 170 ppm, assigned to a large content of carboxyl groups in aliphatic acids of plant and microbial origin and/or amide groups in amino acid moieties. The spectra were integrated in the chemical shift (ppm) resonance intervals of 0–45 ppm (paraffinic carbons), 46–65 ppm (methoxy C from OCH₃, and complex aliphatic carbons), 66–90 ppm (O-aliphatic C, such as alcohols and ethers), 91–145 ppm (aromatic carbon), 145–160 ppm (phenolic carbons), 160–185 ppm (carboxyl, amides and ester) and 185–220 ppm (carbonyls) (Wang et al., 2007; Zhang et al., 2012).

3. Result and Discussion

3.1. Physicochemical characteristics of biochar

The characteristics of biochars originated from different agricultural waste materials are shown in Table 1. Lower temperature pyrolysis process has produced a higher biochar yield and an more enriched volatile matter composition than the high temperature biochars inside biochar product. The volatile compounds are easily degradable compounds, which stimulates the activity of microorganisms in soil as substrate and ends up supplying plant nutrition (Steinbess et al., 2009; Zimmerman, 2012). The biochar yields and volatile contents were gradually reduced by increasing pyrolysis temperatures. Not only the range of pyrolysis temperature, Moreover, the type of feedstock also affected biochar yields and the volatile matter content. Among different biochar types, two types of woody biochars (AB and OB) showed larger variation in volatile content from low temperature to high temperature (from 400 °C to
800 °C) than non-woody biochars (RS and RH), as observed by, and this result is in accordance with other report (Enders et al., 2012). These authors found that the explanation that this attributes to the recalcitrant character of lignin in woody feedstocks can partially resist, which resists still partially pyrolytic decomposition at 400 °C, but not in the range of 950 °C (used for the determination of ash content), increasing the volatile content of woody biochar prepared at relatively low temperatures. For determining the volatile content quantification, low yields and low volatile contents compared to other two kinds of biochar from rice residues (RS and RH). Also, wood original biochar (AB and OB) has less ash content than others, (RS and RH), which is in the accordance with the work of Singh et al., (2010). The biochars derived from rice material (RS and RH) have a high ash content in all temperature ranges, which may have caused and the partial change in of the structure and composition by a possible interaction between organic and inorganic constituents during feedstock pyrolysis, as already reported by composition partially could be occurred according to the report (Elders et al., 2012), in biochar that the biochars, containing above 20% of ashes greater than 20% ash, could be possible interaction between organic and inorganic constituents during feedstock pyrolysis. Overall, those results might be due to the differences in compositions of the original agricultural material since rice plants are enriched with Si, which strongly relates to the ash content of the biochar (Mukome et al., 2013) by the formation of Si-C bonds which increases the aromatic components and recalcitrance of the biochars with increasing pyrolysis temperatures (Guo and Chen, 2014). While in the case of woody feedstocks, while recalcitrant carbons such as lignin content are predominantly contained in woody plants (Liu and Zhang, 2009; Spokas et al., 2009; Joseph et al., 2013). It is reported that the bonds Si-C is probably take part in cross-linking of organic and inorganic compounds such as aromatic groups or
crystallites, and the higher temperature that biochar production is taken place, the SiO$_4^{2-}$ is more dominant relative to SiO$_2$ (Lehmann et al., 2011).

The pH values increased with by higher-temperature, probably as a consequence of the relative concentration of non-pyrolysed inorganic elements, already present in the original feedstocks (Novak et al., 2009). The porosity and surface area represent the main physical properties of biochar, which are strongly connected strongly with the improvement of soil properties such as soil adsorption capacity and water retention abilities, which those has potential to improve soil property (Kalderis et al., 2008), and in particular, taking the advantage of enhanced these properties, the number of works on the application of biochar derived from the rice husk has been reported to an enhancement of these properties in for improvement of the soil quality (Kalderis et al., 2008; Liu and Zhang, 2009; Lei and Zhang, 2013). As shown in Table 1, the biochar production with higher temperatures generally enlarged methylene blue number, I$_2$ absorption, and surface area, compared to than the production with lower temperature (p < .001), and these results are in accordance with other previous work (Gaskin et al., 2008; Liu and Zhang, 2009; Yu et al., 2011).

Regarding of comparison among the variety of origins, the difference in micro-porosity (I$_2$) of biochars between from wood feedstock (AB and OB) and from rice residues (RH and RK) was gradually enlarged as increasing pyrolysis temperature from 500°C to 800°C. In contrast, an apparent difference in surface area was observed. The surface areas of RH and RK reduced at 800°C, while those of AB and OB still had been extending. These decreases in surface areas of RH and RK will be attributed to ash content in biochar, that high content of inorganic ash in biochar filled or blocked access to micropores, resulting in relatively low surface area (Mackay and Roberts, 1982; Song and Guo, 2012).

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

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

Concerning with the difference of the feedstocks in the diagram, the rice material biochars (RS and RH) were distanced from Y axe at 600 °C and 700 °C; whereas the stable reduction of the H/C and O/C in wood biochars (AB and OB) was shown. This result was mainly due to the decrease of C content in RS and RH from
500°C to 600°C, which the shift moved from 45.2% to 40.3% and from 37.5% to 33.8%, in RS and RH, respectively (Table 2). The reduction of carbon content in biochar production could be related to the chemical and physical composition. The change of the physical and structural composition of rice straw biochar between the pyrolysis condition of 500 °C and 700 °C is reported by Guo and Chen, (2014), using SEM-EDS images. For the rice husk biochar made at 500 °C, the silicon was associated with carbon and formed a dense structure, forming Si-encapsulated carbon, meanwhile the silicon component were physically distanced from carbon structure in biochars prepared at the highest temperature for the other made at (700 °C).

3.3. Thermal analysis

Thermal analysis is a useful method to understand the structure of biochar materials. (Kalderis et al., 2014; Mimmo et al., 2014). In our study (Fig. 2), all biochar samples had a similar of the thermal degradation profile, with an increasing weight loss with increasing pyrolysis temperature, has same tendency that biochar produced at 400 °C has the largest proportion of lost weight. The difference among the feedstocks (wood vs. no-wood) was observed in the total weight losses, as observed in the ash content location of the curve of lost weight. The curves of the lost weight in AB and OB were reached up to to a great extent until the 940 percent of total weight, meanwhile the curve in RH and RK reached were stopped around half volume of weight (40-50%), reflecting the higher mineral content. This would be reflected to the high mineral content in rice material, and moreover during charring process this mineral content performs as a barrier to prevent from heat diffusion and the release of the volatile contents (Xu and Chen, 2013).

3.4. Chemical composition with spectra parameters (FT-IR and NMR)
The FT-IR is a great tool to shed light on the shift to observe the shift change of chemical composition. The aliphatic loss process is represented by the band of FT-IR with aliphatic C-H stretching (2950-2850 cm\(^{-1}\)) at increasing temperature from 400\(^\circ\)C to 600\(^\circ\)C (Figure 2), meanwhile, a couple of representative peaks for aromatic carbon appeared more clearly such as C-H stretching (750-900 cm\(^{-1}\) and 3050-3000 cm\(^{-1}\)), C=C (1380-1450 cm\(^{-1}\)), C-C and C-O stretching (1580-1700 cm\(^{-1}\)). As shown by the infrared spectra, charring temperature modifies the functional group, and thus aliphatic C groups decrease but aromatic C increases (Lee et al., 2010). Since longevity of biochar is a matter of debate in relation with the biochar production (Nguyen and Leehman, 2009; Peng et al., 2011), the pyrolysis process of 600 \(^\circ\)C, which creates more recalcitrant character by increasing aromatic compounds, has suitable method in terms of the carbon sequestration. However, when the charring temperature increase over 700 \(^\circ\)C and 800\(^\circ\)C, the intensity of bands decline gradually such as hydroxyl group (3200-3400 cm\(^{-1}\)) and even aromatic bands (1580-1600 cm\(^{-1}\) and 3050-3000 cm\(^{-1}\)). Other works (Yuan et al., 2011) report that the number of bands representing functional groups are present at the lower-temperature biochars (300\(^\circ\)C and 500\(^\circ\)C), and are absent in the biochar-derived by 700\(^\circ\)C. The loss of these functional groups decreases recalcitrant character of biochar, which will be hardly remained after applying it to soil.

The characteristic of feedstock type of biochar has been reflected by the presence of bands around 460 cm\(^{-1}\), 800 cm\(^{-1}\), and 1040-1100 cm\(^{-1}\), assigned to SiO\(_2\), and these bands was shown in all biochars originated from rice materials (RH and RS), showing in the Fig. 3. \textit{The SiO\(_2\) is a major component in chemical structure of rice material, and is typical of recalcitrant property. In plant physiology, the presence of silica is knowingly found as principal component of plant phytoliths and it functions for...}
protection of the plant carbon from degradation (Wilding et al., 1969, Parr, 2006).

Furthermore, in fact, the SiO\(_2\) is a major component in chemical structure of rice material.

In addition, not only the peak of SiO\(_2\) is observed around the 1600 cm\(^{-1}\) in rice biochars (RH and RS), -which assigned to the aromatic compounds, respectively. The shoulder observed around the 1600 cm\(^{-1}\), in rice biochars (RH and RS), -which assigned to the aromatic compounds, respectively. are still retained in RH and RS biochar until the 800°C biochar production.

Guo and Chen (2014) proposed that a novel framework of silicon-and-carbon-couple can contribute a new perspective for evaluating the biochar stability, besides recalcitrant character derived from aromatic carbon compounds. They mention that the structure of encapsulated carbon by silica could protect the biochar against physical and chemical oxidation, and presumably leads to a longer turnover time in soils.

The \(^{13}\)C NMR spectra of different biochars are shown in Fig. 34 (a and b) with similar shape for all biochar materials, dominated by the presence of condensed aromatic signal at 127 ppm. Furthermore, this signal was observed more clearly in all different biochars which are produced at 600°C, and the sharpness of this peak was gradually weaken as temperature increased above 600°C.

Same trend was shown in the shoulder of methoxyl carbons of lignin and carboxylic carbon, at 57 ppm and 190 ppm, respectively. Especially, the biochars, made from rice straw at 800°C (Fig. 3, b) demonstrated the decomposition of shoulder of these ranges.

From this result as well as shown in FT-IR figure, it worth of noting that there is no much need to produce biochar with very high temperature (700°C and 800°C) for preserving stability character, based on the predominance of aromatic structure and keeping higher chemical property with functional groups.

Concerning with lower temperature, the shoulder at around 20 ppm, assigned to easily degradable carbon, appeared in the 400°C-produced biochars, and this shoulder was eliminated in the biochar produced at 500°C. This accords with other’s work
(McBeath et al., 2013) that biochar, produced at 300°-400°C, exhibited broad alkyl signals and carbohydrate band, meanwhile these bands were not detectable over 400°C. As shown in previous section, the biochar, produced at lower temperature, has higher volatile carbon contents. The type of easily degradable compounds possibly contributes to microorganisms in soil as substrate (Khodadad et al., 2011). In this sense, lower temperature is suitable for the biochar utilization for soil fertility. On the contrary, higher temperature pyrolysis selects functional groups and provides aromatic predominant presence in chemical composition, consequently resulting to the formation of recalcitrant structure. However, it should be highlighted that the excess of the high temperature such as 700 °C and 800 °C is not likely suitable and efficient for biochar production, since those biochars reduce recalcitrant character by heat degradation of functional group, and yield lower the biochar production than other biochars.

4. Conclusion

In conclusion, the temperature of pyrolysis process and the type of feedstock change the physico-chemical properties of biochar. In our study, lower temperature pyrolysis has volatile content and ash compounds retained inside biochar structure. Increasing high temperature re-pyrolysis process produces more enhanced the physical property of adsorption property such as large surface area and porosity and the recalcitrant chemical character, reinforced by the function group, are improved. This alteration was strongly shown in wood material biochar (AB and OB). By contrast, rice material biochar (RH and RS) has higher biochar yield during the pyrolysis process than AB and OB, and the property of the biochar product is different from wood material in that the inorganic components is combined with organic moieties in related with the carbon encapsulation by silicon presence, recalcitrant character of functional group and adsorption property due to large surface area and porosity. By contrast, lower
temperature pyrolysis has volatile carbon compounds retained inside biochar structure, which can induce microbial activities in soil. The over-heat production (above 600 °C) showed the disappearance of the functional groups, driven by heat degradation.

5. Acknowledgements

This work was supported in part by JSPS-CSIC bilateral project.

6. References


Lei, O., and Zhang, R.: Effects of biochars derived from different feedstocks and pyrolysis temperatures on soil physical and hydraulic properties. J. Soils Sediments 13, 1561-1572, 2013.


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).

<table>
<thead>
<tr>
<th>samples</th>
<th>temperature (°C)</th>
<th>Biochar Yield (%)</th>
<th>Ash Content (%)</th>
<th>Volatile Content (%)</th>
<th>pH (H₂O)</th>
<th>Methylene Blue adsorption (mg/g DW)</th>
<th>I₂ adsorption (mg/g DW)</th>
<th>BET Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>400</td>
<td>28.3</td>
<td>4.4 ± 0.0</td>
<td>32.43 ± 0.105</td>
<td>7.02 ± 0.08</td>
<td>4.35 ± 0.21</td>
<td>45.04 ± 0.96</td>
<td>11.90</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>16.7</td>
<td>6.5 ± 0.0</td>
<td>32.43 ± 0.105</td>
<td>7.02 ± 0.08</td>
<td>12.04 ± 0.438</td>
<td>97.98 ± 2.765</td>
<td>58.60</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>16.6</td>
<td>7.6 ± 0.1</td>
<td>11.16 ± 0.20</td>
<td>10.04 ± 0.02</td>
<td>5.76 ± 0.448</td>
<td>122.10 ± 1.53</td>
<td>208.76</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>15.8</td>
<td>8.0 ± 0.0</td>
<td>7.72 ± 0.10</td>
<td>10.03 ± 0.02</td>
<td>10.63 ± 0.762</td>
<td>208.52 ± 1.50</td>
<td>418.76</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>15.5</td>
<td>8.6 ± 0.0</td>
<td>6.82 ± 0.102</td>
<td>10.02 ± 0.02</td>
<td>51.82 ± 0.658</td>
<td>298.54 ± 1.70</td>
<td>545.43</td>
</tr>
<tr>
<td>OB</td>
<td>400</td>
<td>35.8</td>
<td>3.6 ± 0.0</td>
<td>32.19 ± 0.105</td>
<td>6.43 ± 0.04</td>
<td>3.90 ± 0.328</td>
<td>38.76 ± 0.04</td>
<td>5.60</td>
</tr>
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<td>500</td>
<td>28.6</td>
<td>5.1 ± 0.1</td>
<td>19.42 ± 0.327</td>
<td>8.10 ± 0.12</td>
<td>5.65 ± 0.547</td>
<td>91.74 ± 0.106</td>
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<td>5.54 ± 0.0</td>
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<td>8.85 ± 0.07</td>
<td>5.54 ± 0.430</td>
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<td>288.65</td>
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<td>17.16 ± 0.216</td>
<td>212.82 ± 1.098</td>
<td>335.64</td>
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<tr>
<td></td>
<td>800</td>
<td>19.1</td>
<td>8.3 ± 0.2</td>
<td>7.98 ± 0.106</td>
<td>9.68 ± 0.03</td>
<td>29.43 ± 0.542</td>
<td>250.32 ± 1.40</td>
<td>398.21</td>
</tr>
<tr>
<td>RH</td>
<td>400</td>
<td>48.6</td>
<td>35.9 ± 0.1</td>
<td>22.00 ± 0.13</td>
<td>6.84 ± 0.03</td>
<td>2.91 ± 0.825</td>
<td>44.10 ± 1.655</td>
<td>193.70</td>
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<td>9.72 ± 0.447</td>
<td>75.44 ± 1.688</td>
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<td>55.1 ± 0.2</td>
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<td>9.52 ± 0.02</td>
<td>13.88 ± 0.109</td>
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<td>256.04</td>
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<td>3.24 ± 0.249</td>
<td>9.62 ± 0.01</td>
<td>34.16 ± 0.34</td>
<td>174.40 ± 3.107</td>
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<tr>
<td>RS</td>
<td>400</td>
<td>39.3</td>
<td>34.0 ± 0.2</td>
<td>22.42 ± 0.109</td>
<td>8.62 ± 0.03</td>
<td>29.32 ± 2.49</td>
<td>74.76 ± 2.64</td>
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<td>29.68 ± 2.84</td>
<td>95.94 ± 1.53</td>
<td>59.94</td>
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<td>82.64 ± 2.02</td>
<td>190.24 ± 1.34</td>
<td>256.97</td>
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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).

<table>
<thead>
<tr>
<th>samples</th>
<th>temperature (°C)</th>
<th>C* (%)</th>
<th>H* (%)</th>
<th>N* (%)</th>
<th>O (%)</th>
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<th>H/C</th>
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<tbody>
<tr>
<td>AB</td>
<td>400</td>
<td>70.21 ± 0.245</td>
<td>4.13 ± 0.01</td>
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<td>20.65 ± 0.13</td>
<td>0.22</td>
<td>0.71</td>
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<td></td>
<td>500</td>
<td>79.12 ± 0.00</td>
<td>2.65 ± 0.09</td>
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<td>12.04 ± 0.10</td>
<td>0.11</td>
<td>0.40</td>
</tr>
<tr>
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<td>600</td>
<td>81.54 ± 0.105</td>
<td>1.96 ± 0.02</td>
<td>0.46 ± 0.00</td>
<td>13.63 ± 0.326</td>
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<td>0.29</td>
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<tr>
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<td>700</td>
<td>82.32 ± 1.439</td>
<td>1.21 ± 0.05</td>
<td>0.41 ± 0.02</td>
<td>16.34 ± 0.768</td>
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<td>OB</td>
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<td>70.52 ± 0.24</td>
<td>3.70 ± 0.02</td>
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<td>21.54 ± 0.245</td>
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<td>0.31 ± 0.00</td>
<td>15.04 ± 0.707</td>
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<tr>
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<td>0.69 ± 0.06</td>
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<td>17.32 ± 0.12</td>
<td>0.16</td>
<td>0.10</td>
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<td>RH</td>
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<td>600</td>
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<td>0.37 ± 0.01</td>
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<td>0.17</td>
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<tr>
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<td>700</td>
<td>38.81 ± 0.546</td>
<td>0.46 ± 0.04</td>
<td>0.26 ± 0.02</td>
<td>12.76 ± 0.20</td>
<td>0.25</td>
<td>0.14</td>
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<tr>
<td></td>
<td>800</td>
<td>40.44 ± 0.768</td>
<td>0.28 ± 0.01</td>
<td>0.22 ± 0.00</td>
<td>2.769 ± 0.04</td>
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<tr>
<td>RS</td>
<td>400</td>
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<td>2.80 ± 0.10</td>
<td>1.22 ± 0.01</td>
<td>12.02 ± 0.106</td>
<td>0.18</td>
<td>0.67</td>
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<tr>
<td></td>
<td>500</td>
<td>37.548 ± 0.22</td>
<td>0.93 ± 0.03</td>
<td>0.61 ± 0.01</td>
<td>8.64 ± 0.33</td>
<td>0.17</td>
<td>0.30</td>
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<tr>
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<td>33.878 ± 1.02</td>
<td>0.60 ± 0.07</td>
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<td>13.768 ± 0.32</td>
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<td>0.25 ± 0.01</td>
<td>3.74 ± 0.04</td>
<td>0.10</td>
<td>0.10</td>
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</tbody>
</table>
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 =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 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. - 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 rice residues; RH (rice husk) and RS (rice straw)
Fig. 3a. - FT-IR spectra of biochars of wood materials; AB (apple tree) and OB (oak tree)

Fig. 3b. - 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
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AUTHORS
Keiji Jindo1,2*, Hideki Mizumoto3, Yoshito Sawada2, Miguel A. Sanchez-Monedero1, and Tomonori Sonoki3

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Physical and Chemical Characterizations of Biochars Derived from Different Agricultural Residues

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Phone: +34 968396364
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Abstract

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

Keywords: biochar; pyrolysis; NMR; carbon sequestration; crop residues
1. Introduction

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

The biochar physicochemical properties can drive changes in the soil nutrient and C availability, and provide physical protection to microorganisms from predators and desiccation. This may finally promote the alteration of the microbial diversity and the taxonomy of the soil (Lehman et al., 2011). The biochar derived from relatively low-temperature pyrolysis is characterized by a high content of volatile matter that contains decomposable substrates, which can contribute to plant growth (Robartson et al., 2012; Mukherjee and Zimmerman, 2013). On the other hand, the structure of the biochar derived from high-temperature pyrolysis is characterized by a large surface area and high-aromatic-carbon content, which could promote the
adsorption capacity (a desirable property for bioremediation) as well as the recalcitrant character (for carbon sequestration) (Lehmann, 2007).

The type of feedstock material is also another important factor that determines the final application of the biochar and its effect in soil, to guide the proper orientation of application, because its properties are of biochar will be affected by the nature of the original material, and consequently its effect in soil. For instance, the soil cation-exchange capacity of is enhanced more by manure-based biochars is higher than that of wood (Eucalyptus) biochar (Singh et al., 2010), meanwhile the treatment of the soil with woodchip biochar resulted in higher saturated hydraulic conductivities than that treated with manure-based biochar treatment (Lei and Zhang, 2012).

The aim of our study is to optimize the physicochemical characteristics of biochar for its use in agriculture by combining-investigating different pyrolysis conditions and the selection of different agricultural wastes used as feedstocks. To achieve this aim, the thermo-chemical properties of the biochars obtained at different temperatures (400–800 °C) were evaluated. Rice husk (RH) and rice straw (RS) were used in our work as original the starting materials, since the global amounts of residues from rice crops (Oryza sativa L.) are is 0.9 Gt for per a-year, i.e., which constitutes the 25% of the total amount of the whole global agricultural residues produced in the world (Knoblauch et al, 2011). More Also, the research is being conducted on the properties of characteristic of biochars derived from orchard residues and pruning woodchips of apple tree (AB) (Malus pumila), than are taking-place, comparing with that with hard-wood biochar derived from the of oak tree (OB), (Quercus serrata). The carbonization of pruning woodchip could may be considered as an alternative waste management not only for the reduction of hazardous materials such as pesticide remnant (Suri and Horio, 2010) but also for soil sequestrating carbon
sequestration in soil. Although several works studies have been recently proposed on the
use of pruned-biochar as a soil amendment have been recently published (Fellet et al.,
2011: Alburquerque et al., 2013), the reports on the evaluation of the pyrolysis process
on this feedstock are hardly reported.

2. Materials and Methods

2.1 Biochar Preparation from Agricultural Residues

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

2.2 Biochar Chemical Analysis of Biochar

After the pyrolysis process, all samples were grounded and sieved to less than 0.5 mm
in diameter. The biochar yield was calculated as the proportion of the weight of
pyrolysis product to the original material. The determination of the volatile matter and
ash content was conducted according to the American Society for Testing and Materials
(ASTM) D1752-84, which is recommended by the International Biochar Initiative.
The volatile matter was thus determined by measuring weight loss that
following the combustion of about 1 g of charcoal in a crucible at 950 °C. With
Following the same procedure as the volatile matter, the ash content was
determined at 750 °C. The pH of each mixture (pH at 1:10, w/v ratio) was measured
with the MP220 pH-meter. Micro- and meso-porosity were evaluated by the iodine ($I_2$) and methylene blue (MB) adsorption capacity, respectively, following a previously proposed methodology (used by Gaspard et al., 2007). The specific surface area was determined using $N_2$ sorption isotherms run on an automated surface area. The specific surface area distribution was taken from the adsorption isotherms, using the equation of Brunauer–Emmett–Teller (BET) equation (Zhang et al., 2011).

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

2.2.2 Thermal Analysis
The thermal analysis of the biochars was performed by using an SDT-2960 simultaneous DSC-TGA thermal analyzer (TA instruments) under static-air atmosphere with the following temperature ramp, e.g., a temperature equilibrating at 30 ºC, followed by a linear heating (at a rate of 5 ºC min$^{-1}$) from 30 to 105 ºC, an isotherm for 10 min, and then continued ramping of 5 ºC min$^{-1}$ from 105 to 680 ºC.

2.2.3 Infrared Spectra
Infrared spectra were recorded on a Varian 670-IR (Agilent Technologies Inc., CA) using the pellet technique by mixing 1 mg of dried biochar with 300 mg of pre-dried and pulverized spectroscopic-grade KBr (from Merck & Co., Whitehouse Station, NJ). The following broad-band assignment was used (Chen and Chen, 2009;
Haslinawati et al., 2011; Novak et al., 2010; Peng et al., 2011; Yuan et al., 2011; Wu et al., 2012; Guo and Chen, 2014): 3400 to 3410 cm$^{-1}$, H-bonded O–H stretching vibrations of hydroxyl groups from alcohols, phenols, and organic acids; 2850 to 2950 cm$^{-1}$, C–H stretching of alkyl structures; 1620–1650 cm$^{-1}$, aromatic and olefinic C=C vibrations, C=O in amide (I), ketone, and quinone groups; 1580 to 1590 cm$^{-1}$, COO$^-$ asymmetric stretching; 1460 cm$^{-1}$, C-H deformation of CH$_3$ group; 1280–1270 cm$^{-1}$, O-H stretching of phenolic compounds; and three bands around 460 cm$^{-1}$, 800 cm$^{-1}$, and 1000–1100 cm$^{-1}$, bending of Si-O stretching.

2.2.4 Solid-state Nucleic Magnetic Resonance spectroscopy (NMR) Spectroscopy

Cross-polarization magic angle spinning (CPMAS) $^{13}$C nuclear magnetic resonance ($^{13}$C-NMR) spectra were acquired from the solid samples with a Varian 300, equipped with a 4-mm-wide bore MAS probe, operating at a $^{13}$C resonating frequency of 75.47 MHz. The assignment of the following peaks and broads was used (Brewer et al., 2009; Calvero et al., 2011).

The peak around 30 ppm, is assigned to considered as content of the methylenic chains and/or CH$_2$ groups deriving from various lipid compounds and plant waxes; the two peaks at 55 ppm and 70 ppm were assigned to methoxy and O-alkyl groups, characteristic of the relatively easily biodegradable compounds such as remaining cellulose, and hemicellulose; the broad band around 130 ppm was assigned to alkyl substitutions in the p-hydroxy phenyl ring of the cinnamic and p-coumaric units of both lignin and suberin biopolymers, as well as to both partially degraded lignin structures and condensed aromatic and olefinic carbons; the sharp peak at 170 ppm assigned to the large content of carboxyl groups in the aliphatic acids of plant and microbial origin and/or amide groups in amino acid moieties. The spectra were integrated in the chemical shift (ppm) resonance intervals of 0–45 ppm (paraffinic carbons), 46–65 ppm (methoxy C
from OCH₃, and complex aliphatic carbons), 66–90 ppm (O-aliphatic Cᵢ such as alcohols and ethers), 91–145 ppm (aromatic carbon), 145–160 ppm (phenolic carbons), 160–185 ppm (carboxyl, amides, and ester) and 185–220 ppm (carbonyls) (Wang et al., 2007; Zhang et al., 2012).

3. Result and Discussion

3.1. Biochar Physicochemical Characteristics of Biochar

The characteristics of the biochars originated from different agricultural wastes are shown in Table 1. Low-temperature pyrolysis produced a higher biochar yield and an enriched volatile-matter composition than the high-temperature biochars. The biochar yields and volatile contents were gradually reduced as the pyrolysis temperature increased. Moreover, the type of feedstock also affected the biochar yields and the volatile-matter content. Among the different biochar types, woody biochars (AB and OB) showed a larger variation in the volatile content from low-temperature to high-temperature (from 400°C to 800°C) than non-woody biochars (RS and RH), as previously observed (by Enders et al., 2012). These authors found that the recalcitrant character of lignin in woody feedstocks can partially resist pyrolytic decomposition at 400°C, but not at temperatures as high as 950°C (for example, used for the determination of ash content); this leads to an increasing in the volatile content of the woody biochar prepared at relatively low temperatures. The biochars derived from rice material (RS and RH) have showed a high ash content at all temperature ranges, which may be the cause for the partial change in the structure and composition promoted by a possible interaction between organic and inorganic constituents during the feedstock pyrolysis as already reported (by Elders et al., 2012); in the biochars that containing an amount of ash larger than above 20% of ashes, Rice plants are
enriched-rich within Si; this may be due, which strongly relates to the ash content of the biochar (Mukome et al., 2013), which favors the formation of the Si-C bonds, thereby increasing the number of aromatic components and recalcitrance of the biochars as a result of an increase in the pyrolysis temperatures (Guo and Chen, 2014). In the case of woody feedstocks, recalcitrant carbons such as lignin content are the main component predominantly contained in woody plants (Liu and Zhang, 2009; Spokas et al., 2009; Joseph et al., 2013).

The pH values increased with temperature, probably as a consequence of the relative concentration of non-pyrolyzed inorganic elements, already present in the original feedstocks (Novak et al., 2009). The porosity and surface area, which are critical factors for the improvement of soil properties such as soil adsorption capacity and water retention abilities (Kalderis et al., 2008). The application of the RH biochar derived from the rice husk has been reported to enhance these properties in the soil (Kalderis et al., 2008; Liu and Zhang, 2009; Lei and Zhang, 2013). As shown in Table 1, the biochar production at higher temperatures generally enlarged leads to an increase in the MB-methylene blue number, I$_2$ absorption, and surface area, compared to the production at lower temperatures (p < .001); this is in line and these results are in accordance with other previous studies (Gaskin et al., 2008; Liu and Zhang, 2009; Yu et al., 2011). In addition, Regarding of comparison among the variety of origins, our data showed that the difference in the micro-porosity (I$_2$) of between the biochars obtained from wood feedstock (AB and OB) and those from rice residues (RH and RK) was gradually enlarged as the increasing pyrolysis temperature from increased from 500 °C to 800 °C. In contrast, an apparent difference in surface area was observed. The surface areas of RH and RK reduced at 800 °C, while those of AB and OB still had been expanded. The former
behavior, as decreases in surface area was of RH and RK will be attributed to the ash content in the biochar, which that high content of inorganic ash in biochar filled or blocked the access to micropores, resulting in a relatively low surface area (Mackay and Roberts, 1982; Song and Guo, 2012).

3.2. Analytic Elements

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

Because of the high temperature of the charring process, Regarding with the H/C/ and O/C ratios, (Table 2) are shows the reduced, as a result of these ratios with charring temperature, being attributed to the dehydration and decarboxylation reactions. The change of the O/C ratio in the range from 400°C to 500°C range was remarkably changed according to the following observed in the order: of RS > RK > AB > OB. Yang et al., (2007) and Khodadad et al., (2011) found that the biochar made derived from wood and at higher temperatures is are less biologically labile, because it contains a containing relatively higher proportion of more aromatic organic matter, - compared to that of other biochars prepared from agricultural residues.
and at lower temperatures. As shown in the van Krevelen diagram (Fig. 1), the constancy of the reduction in the H/C and O/C ratios steadily diminish as the temperature increases, increasing temperature are observed, reflecting the loss of easily degradable carbon compounds such as volatile matters. At the parallel Similarly, a lower C/O ratio in biochar with higher temperatures indicates an arrangement of the aromatic rings (Spokas et al., 2010), which forming very stable crystal graphite-like structures with high stability (Wu et al., 2012; Dong et al., 2013).

Concerning A comparison of the with the difference of the feedstocks in the diagram indicates that, the rice materials RS and RH biochars (RS and RH) were are distanced from the Y axe at 600 °C and 700 °C; whereas the H/C and O/C ratios in the AB and OB biochars show at the stable reduction of the H/C and O/C in wood biochars (AB and OB) was shown. The reduction of the carbon content in the biochar production could may be related to the chemical and physical composition. In particular, a previously proposed SEM-EDS analysis suggested a The change of in the physical and structural composition of the rice straw RS biochar obtained at between the pyrolysis temperatures condition of 500 °C and 700 °C is reported by Guo and Chen (2014), using SEM-EDS images (Guo and Chen, 2014). For the rice husk biochar made at 500 °C, In addition, the silicon of the RH biochar obtained at 500 °C was associated with the formation of a carbon and formed a dense carbon structure (forming Si-encapsulated carbon); in contrast, meanwhile the silicon component were physically distanced from carbon structure in the biochars prepared at the highest temperature (700 °C), the silicon component was physically distanced from the carbon structure.

3.3. Thermal Analysis

Thermal analysis is a useful method to understand study the structure of biochar materials. (Kalderis et al., 2014; Mimmo et al., 2014). In our this work study (Fig. 2),
all biochar samples had showed a similar thermal-degradation profile (Fig. 2), with an increasing weight loss proportionally increasing with increasing pyrolysis temperature of pyrolysis. In this respect, a clear difference among the feedstocks (wood vs. non-wood) was observed in the total weight losses, as observed in the ash content, i.e., the curves of the lost weight in of AB and OB, and RH and RK reached was up to 90% and 40–50% percent of the total weight, respectively; meanwhile, this behavior the curve in RH and RK reached around half volume of weight (40–50%), reflecting the higher mineral content in rice materials. In addition, and moreover during charring process, their mineral component content performs functions as a barrier that prevents from the diffusion of heat diffusion, and therefore the release of the volatile components during the charring process (Xu and Chen, 2013).

3.4. Chemical Composition with Spectra Parameters (FT-IR and NMR)

The FT-IR is a great tool to observe the shift change of chemical composition. The aliphatic loss process is represented by The FT-IR band at 2950–2850 cm\(^{-1}\) (which appears in the temperature range of 400 and 600 °C) was assigned to the FT-IR with aliphatic C-H stretching (2950–2850 cm\(^{-1}\)) at increasing temperature from 400°C to 600°C (Figure 2); this indicates an aliphatic loss. In addition, meanwhile, the typical representative peaks of for aromatic carbon appeared more clearly; these were appeared more clearly assigned to the such as C-H stretching (750–900 cm\(^{-1}\) and 3050–3000 cm\(^{-1}\)), C=C (1380–1450 cm\(^{-1}\)), C-C and C-O stretching (1580–1700 cm\(^{-1}\)). These data suggest that As shown by the infrared spectra, the charring temperature can modifies the functional groups, leading to a decrease in, the and thus aliphatic C groups and decrease an increase in but aromatic C increases (Lee et al., 2010). Since the biochar longevity of biochar is a matter of debate in relation with the its biochar
production is still a matter of debate (Nguyen and Lehman, 2009; Peng et al., 2011), the pyrolysis process of at 600 °C, which leads to a higher more recalcitrant character by increasing the number of aromatic compounds, has a suitable method in for terms of the carbon sequestration. However, when the charring temperature increases to values larger than over 700 °C and – 800 °C, the intensity of the bands such as that of decline gradually such as the hydroxyl groups (3200 – 3400 cm\(^{-1}\)) and even aromatic bands (1580 – 1600 cm\(^{-1}\) and 3050 – 3000 cm\(^{-1}\)) gradually diminishes. Other Previous studies works (Yuan et al., 2011) have shown that the number of bounds representing functional groups are present in biochars obtained at the lower temperature biochars (300 °C and 500 °C), and are absent in those derived by biochar derived by at 700 °C. In particular, The characteristic of feedstock type of biochar has been reflected by the presence of bounds around 460 cm\(^{-1}\), 800 cm\(^{-1}\), and 1040 – 1100 cm\(^{-1}\), which were assigned to SiO\(_2\), reflects the nature of the feedstock type; and these bands were observed in shown in all the RH and RS biochars originated from rice materials (RH and RS), showing in the (Fig. 3–b). In plant physiology, the presence of silica is knowingly known to be found as the most critical principal component of for plant phytoliths, as phytoliths and it functions for protection of the plant carbon from degradation (Wilding et al., 1969; Parr, 2006). In fact, SiO\(_2\) is a major component in the chemical structure of rice material. – The shoulder observed around 1600 cm\(^{-1}\) in rice–the RH and RS biochars (RH and RS), which was assigned to the aromatic compounds, is still present retained at temperatures as high as until the 800 °C during the biochar production. Guo and Chen (2014) proposed that a novel framework of silicon–and carbon framework that couple may provide can contribute a new perspective for the evaluation of the biochar stability, in addition to the recalcitrant character derived from the aromatic carbon compounds. In particular, They
mention that the structure of encapsulated carbon by silica could protect the biochar against physical and chemical oxidation, and presumably leading to a longer turnover time in soils.

The $^{13}$C NMR spectra of different biochars (are shown in Fig. 3 (a and b)) with similar show shape for all biochar materials, a strong dominated by the presence of condensed aromatic signal at 127 ppm. Furthermore, This signal was becomes more intense in the observed more clearly in all different biochars which are produced at 600°C; however, and the sharpness of this peak was gradually weaken as the temperature increased (above 600°C), this peak loses sharpness. Same trend was shown in the shoulder of the methoxyl carbons of lignin and that of carboxylic carbons, at 57 ppm and 190 ppm, respectively, shows a similar trend, i.e., Especially, the biochars made from rice straw at 800°C (Fig. 3, b) demonstrated a the decomposition of this shoulder was observed for the RS biochars obtained at 800 °C (Fig. 3b). Of these ranges, These results along with those of the is result as well as shown in FT-IR analysis suggest that there is no much need to produce biochar with very high temperature (700–800°C and 800°C) may affect for preserving the chemical properties of the functional groups and the stability character of the biochars, as a result of based on the predominance the formation of aromatic structures and keeping higher chemical property with functional groups.

Concerning with lower temperature, The shoulder observed at around 20 ppm, which was assigned to easily degradable carbon compounds, appeared in for the biochars produced at $\sim$400°C-produced biochars; this shoulder was not detected eliminated in the biochars produced at 500°C. This accords is in agreement with previous studies other’s work (McBeath et al., 2013) that have shown that the biochars produced at temperatures of $\sim$300–$\sim$400°C exhibited broad alkyl signals and carbohydrate bands; meanwhile these bands were not detected above over 400°C.
As shown in the previous section, the biochars produced at lower temperatures contain a large amount of higher volatile carbon contents. This type of easily degradable compounds possibly contributes to microorganisms in soil as substrate (Khodadad et al., 2011). In this sense, a lower temperature may be more suitable for the application of the biochars for the improvement of utilization for soil fertility. On the contrary, higher-temperature pyrolysis selects functional groups and provides aromatic predominant presence in chemical composition, consequently resulting in the formation of recalcitrant structure. However, it should be remarked that should be highlighted that the excess of the high temperatures as high as such as 700–800°C are not likely suitable for an efficient biochar production for biochar i.e., the heat degradation of the functional groups—production, since they may reduce the biochars reduce recalcitrant character, thus resulting in a by heat degradation of functional group, and lower biochar yield lower the biochar production than other biochars.

4. Conclusion

The data presented in this work clearly showed that both pyrolysis temperature of pyrolysis and the type of feedstock drive the physico-chemical properties of the biochars. In particular, an increase in the temperature improved the enhanced physical property of adsorption properties such as large surface area and porosity, and the recalcitrant chemical character in woody material biochars (AB and OB). In By contrast, rice material biochar (RH and RS) has shows a higher biochar yield during the pyrolysis process than that of AB and OB. In addition, and the properties of the rice-material biochar products are different from woody material biochars, i.e., the inorganic components are combined with organic moieties as a consequence of the in related with the carbon encapsulation promoted...
by silicon presence. Finally, the over-heat production (temperature above 600 °C) showed causes the decomposition disappearance of the functional groups driven by heat degradation.

5. Acknowledgements

This work was partly supported in part by the JSPS-CSIC bilateral project.
<table>
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<th>samples</th>
<th>temperature (°C)</th>
<th>Biochar Yield (%)</th>
<th>Ash Content (%)</th>
<th>Volatile Content (%)</th>
<th>pH (H$_2$O)</th>
<th>Methylene Blue (mg/g DW)</th>
<th>I$_2$ adsorption (mg/g DW)</th>
<th>BET Surface Area (m$^2$/g)</th>
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<td>AB</td>
<td>400</td>
<td>28.3</td>
<td>4.4 ± 0.0</td>
<td>32.4 ± 0.1</td>
<td>7.02 ± 0.08</td>
<td>4.4 ± 0.2</td>
<td>45.0 ± 2.6</td>
<td>11.9</td>
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<td>298.5 ± 1.7</td>
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<td>12.6 ± 2.0</td>
<td>190.2 ± 1.3</td>
<td>256.97</td>
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Table 2. Elemental compositions of biochars derived from different feedstocks; AB (apple tree branch), OB (oak tree), RH (rice husk), and RS (rice straw).

<table>
<thead>
<tr>
<th>samples</th>
<th>temperature (°C)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>O (%)</th>
<th>O/C</th>
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Figure legends

Fig. 1. Van Krevelen diagram of the biochars derived 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 CPMAS-NMR of the biochars obtained from (a) of wood materials (AB (apple tree) and OB (oak)) 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.
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).