

Article

Temperature Effects on Properties of Rice Husk Biochar and Calcinated Burkina Phosphate Rock

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Abstract: Rice husk biochar (RHB) and phosphate rock (PR) are locally accessible resources that poor farmers in Sub-Saharan Africa (SSA) can utilize to increase rice productivity. However, biochars are variable depending on feedstock, pyrolysis temperature, and duration. Phosphate rocks from SSA are of low solubility. The goal of this study was to determine whether pyrolysis of rice husk (RH), calcination of PR, and the calcination/pyrolysis of a RHB-PR mixture at 300 °C, 500 °C, and 700 °C can increase formic acid (FA)- extractable phosphorous (P). The properties of these RHBs were compared to the properties of RHB produced through a simple farmer-friendly pyrolysis technique termed “Kun-tan”. Properties of calcinated PR were also compared to the raw PR. Quartz formed from amorphous SiO₂ during RH pyrolysis and was the dominant mineral phase in the biochars, irrespective of the pyrolysis temperature. Formic acid-extractable P content, pH, and ash content of the biochars increased with increasing pyrolysis temperature. At 700 °C, FA-extractable P content of the RHB was 219% more than the feedstock. Hydroxyapatite and quartz were the dominant minerals in the PR irrespective of calcination temperature, indicating that hydroxyapatite and quartz were stable to at least 700 °C. Rather, calcination decreased the FA-extractable P content of the PR.

Keywords: rice husk biochar; phosphate rock; phosphorous; quartz; hydroxyapatite

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1. Introduction

Large areas of the semi-arid regions of West Africa are covered by soils underlain by ferruginous crusts which are sesquioxide rich, humus poor, and kaolinitic. They are regarded amongst the least fertile soils in the tropics [1]. According to Amatekpor [2], the soils of northern Ghana developed over two main geological formations: the Birimian (Middle Pre-Cambrian) and the Voltaian (Lower Paleozoic). The soils formed from the weathered products of the Birimian rocks are relatively fertile, because the Birimian formation contains considerable amounts of weatherable primary minerals [1]. However, the soils developed from the weathered products of the Voltaian rocks are humus poor, rich in iron and aluminium oxy-hydroxides, and have a mineralogy dominated by quartz and low-activity clays with low effective cation exchange capacity [1,3–5]. Consequently, the soils of large areas of northern Ghana are severely deficient in phosphorous (P), which is often the limiting factor for rice production in inland valleys [6].

Chemical fertilizer application rates in Sub-Saharan Africa (SSA) are typically only one-sixth of the amount applied in Asia, due to the high price [7–9]. In Ghana, the implementation of a national fertilizer subsidy program has resulted in increased fertilizer use [10,11]. However, fertilizer use among rice farmers varies depending on rice ecology. Nearly 100% of farmers within irrigated rice ecologies apply chemical fertilizer, while only 67% of farmers on lowlands (78% of total harvested area) use fertilizer [12]. According to Ragasa et al. [11], among farmers who use fertilizer, adequate nitrogen fertilizer is

applied in Ghana, with some coastal savanna areas like Kpong overapplying N. However, P application is only about half the recommended rate.

Socioeconomic constraints, policy distortions, and product availability are among the factors limiting fertilizer use and P application in particular [3,13]. In Ghana, compound fertilizers (15-15-15 and 23-10-5), NPK, and nitrogenous fertilizers like urea and sulfate of ammonia are covered by the Government's fertilizer subsidy program and are available on the market; however, phosphate fertilizers like Single Super Phosphate (SSP) and Triple Super Phosphate (TSP) are difficult to find and are not covered by the subsidy program. Phosphorous and potassium are, therefore, typically applied to rice farms as part of compound fertilizers (15-15-15 or 23-10-5). Hence, both affordability and availability of P fertilizers are challenges to rice production. A potential approach to solving the P problem that addresses affordability and availability will be to re-evaluate the suitability of locally available P resources.

Rice straw, rice husk (RH), and cow dung, among others, have been mentioned as materials that can easily be accessed by small-scale, resource-poor farmers [14–16]. These materials have been shown to be effective in increasing rice yields, especially when combined with mineral fertilizers [17].

By 2011, the global mass of residues from rice crops was estimated at 0.9 Gt per year, equivalent to 25% of the total amount of the global agricultural residues [18]. Although estimates of rice husk residues in Ghana are not available, it is common to see rice husk piles close to rice mills in the major rice growing areas. If there is a way to return this residue to farmers' fields as soil amendment, significant improvement in soil fertility may result.

There is increasing interest in the use of biochar, the C-rich product of biomass pyrolysis, as a soil amendment. However, the C content of biochars and other properties of biochars vary greatly depending on feedstock and pyrolysis conditions [19–21]. In an evaluation of 16 biochars, C content was found to vary from 1.4% (Turkey manure + woodchip) to 84% for Macadamia shell [22]. The same study found the total nitrogen content to vary from 0.1% for wood pellet biochar to 2.7% for peanut hull biochar. Similarly, proximate analysis, elemental analysis, and NMR spectroscopy showed that aromatic C content increased with extent of pyrolysis [20]. Jindo et al. [19] evaluated the physicochemical properties of rice husk and rice straw biochars at different pyrolysis temperatures and reported a decrease in H, N, biochar yield, and volatile content with increasing temperature, while pH and surface area increased with increasing pyrolysis temperature.

Due to the abundance of RH, locally produced rice husk biochar (RHB) could be an inexpensive soil amendment available to farmers in northern Ghana. However, because of the wide variation in biochar quality, uncertainty exists about the impact of locally produced RHB on soil properties and crop productivity. Furthermore, large-scale application of biochar by farmers will require a farmer-friendly and affordable pyrolysis technique that can produce the quantities required for soil amendment. Therefore, this study compares the mineralogical and chemical properties of laboratory biochars produced at 300 °C, 500 °C, and 700 °C to a simple farmer-friendly, variable temperature pyrolysis technique termed "Kun-tan".

Phosphate rock (PR) resources are plentiful in SSA, especially in some of the countries that share borders with Ghana. Phosphate rocks are the basic materials used in the production of all phosphorus fertilizers. According to Lindsay and Vlek [23], the three commonly occurring mineral deposits of phosphorous are: apatite (calcium phosphate), crandallite (aluminium phosphate), and millisite (iron and aluminium phosphate). Although the total PR production in Africa accounts for 28.5% of total PR production in the world, Africa consumes only 2.8%. The most important factor accounting for the low utilization of some of Africa's PR is low solubility [14]. Phosphate rocks are mostly acid treated to produce water-soluble phosphorous fertilizers, which are the phosphate fertilizers used in crop production [24]. Increased solubility of PR could be achieved by some low-cost solubilization techniques suggested in the literature including: (1) composting with organic materials,

(2) solubilizing PR with fungi, and (3) low/high temperature heating, also known as calcination/calcining [24–28].

The agronomic potential of Togo rock phosphate (TRP) and 50% acidulated Togo rock phosphate (PAPR) used in northern Ghana was found to be low [29]. Abekoe and Tiessen [30] found the agronomic effectiveness of PAPR from Togo to be 63% of single super phosphate (SSP). Much of the research to improve the solubility of PR in northern Ghana has focused on Togo PR [27,29,30]. Furthermore, the literature suggests much of the research on PR solubility in northern Ghana and West Africa as a whole has focused on partial acidulation [29–31]. This work focuses on Burkina PR (BPR) and thermal calcination and calcination during the pyrolysis of RHB as a continuation of efforts to replace expensive imported phosphate fertilizers with locally available P resources.

When PR is dominated by crandallite and millisite, calcination is particularly effective, because crandallite and millisite dehydrate to form an amorphous phase upon heating, thus becoming more soluble [32]. Although Bolan et al. [24] also mentioned thermal treatment or calcination as a means of partially decomposing PR, they did not specify if thermal treatment was applicable to all types of PR. Another uncertainty in calcination of PR is the exact temperature of calcination. Rhenania phosphate as produced in Germany is a calcinated blend of PR, sodium carbonate, and silica at 1200 °C to 1300 °C [24], whereas Gilkes and Palmer [32] produced calcinated phosphorous fertilizers that differed in plant growth and citrate-extractable P at temperatures up to 1050 °C. It is therefore not certain if calcination of apatite-dominated PR can further enhance its solubility. Thus, evaluating BPR to determine whether calcination will increase P solubility is one of the goals of this study.

Finally, we are interested to know whether calcining BPR during the pyrolysis of rice husks to produce RHB will increase P solubility, and hence, plant-available P.

The objectives of this study are to determine the chemical and mineralogical properties of BPR before and after it is calcined during pyrolysis of RHB, and to elucidate the effect of BPR calcination on plant-available P. Specifically, we compared the chemical and mineralogical properties BPR calcined at 300 °C, 500 °C, and 700 °C during the production of RHB to the raw BPR and determined the effects of pyrolysis temperature and calcination temperature on 2% formic acid-extractable P, which is used as a proxy for “plant-available P” [32]. Additionally, this study compared the mineralogical and chemical properties of biochars produced at 300 °C, 500 °C, and 700 °C in a laboratory furnace with biochars produced by the farmer-friendly “Kun-tan” method.

2. Materials and Methods

2.1. Feedstock and Biochar Preparation

Rice husk (RH) feedstock in its natural state was packed into a steel box and pyrolyzed in a muffle furnace for two hours at three temperatures (300 °C, 500 °C, and 700 °C). Samples were prepared in triplicate. Biochar was also produced using a “Kun-tan” maker (Figure 1). The Kun-tan process involves four basic steps: (1) fire is set, (2) the fire is covered with a Kun-tan maker, (3) rice husk is spread around the Kun-tan maker, and (4) the material is churned occasionally after pyrolysis commences. The material changed color from brown to black, indicating completion of the pyrolysis. The temperature fluctuated throughout the process.



Figure 1. The Kun-tan (Biochar)maker. Honma Co. Ltd. Nigata, Japan.

2.2. Calcination of Burkina Phosphate Rock (BPR)

Burkina phosphate rock, from the Kodjari deposit in Burkina Faso, and sold as a PR powder was used for this study. Calcination of phosphate rock was done by placing the phosphate ore in a steel box and heating at 300 °C, 500 °C, and 700 °C in a muffle furnace for two hours.

2.3. Mineralogical Analysis

Samples were thoroughly ground with a mortar and pestle, after which a spatula was used to homogenize the samples. Samples were then loaded into sample holders as randomly oriented powder and pressed with glass slides. Mineralogical composition of RHB, BPR, and RHB-BPR mixtures was determined by X-ray diffraction analysis from 10 to 80° 2 θ for RHB, and 10 to 100° 2 θ for BPR and RHB-BPR mixtures, with a Siemens D5000 X-ray diffractometer using Cu K α radiation. The tube was energized at 40 kV and 30 mA and the spectrometer was operated in step scan mode with a step size of 0.05° 2 θ and a dwell time of 7 s per step. Fixed 1.0° divergence and 3.0° anti-scattering slits were used with a scintillation counter. The XRD patterns were analyzed using JADE v9.0 (Materials Data Inc., Livermore, CA, USA).

2.4. Chemical Analysis

Elemental composition of the phosphate ore was determined with a Philips PW 2404 X-ray fluorescence (XRF) spectrometer equipped with a rhodium X-ray tube operated at 3600 W and flushed with helium gas.

Biochar pH was determined using a biochar-to-deionized water ratio of 1:15, and the pH of phosphate rock powder was measured in deionized water using a ratio of 1:2. The pH was measured using a glass electrode and an Orion Star A215 pH meter.

Carbon, hydrogen, nitrogen, and sulphur (C, H, N, S) concentrations of RHB and PR were determined using a C/N combustion analyzer (Vario Microcube, Elementar Langensfeld, Germany) after samples were ground. The ash content of the biochar was determined by weighing after the ashing of feedstock and biochars at 600 °C.

Formic acid-extractable P (FA-P) content was determined according to the method described by Wang et al. [33]. The 2% formic acid-extractable P procedure involves weighing 0.35 g of RHB, BPR, and RHB-BPR mixtures into 50-mL extraction bottles before adding 35 mL of extractant and shaking for 30 min. Solution and solid phases were separated by

centrifugation (using the Sorval Centrifuge, with S34 rotor at 15,000 rpm for 10 min). The supernatant was filtered through Whatman No. 41 filter paper. Filtrate P concentrations were determined by the molybdate colorimetric method at 420 nm [33].

All chemical analyses were done in triplicates. The significance of temperature effects on selected chemical properties of RHB and BPR was assessed using the ANOVA procedure in SAS (SAS Institute, Cary, NC, USA). Mean comparisons were done using LSD procedure and all tests of significance were assessed using an alpha of 0.05.

3. Results and Discussion

3.1. Mineralogical Properties of RHB, BPR, and RHB-BPR Mixture

The X-ray diffraction patterns of the rice husk feedstock showed three peaks (Figure 2). The XRD analysis showed a main peak at 3.93 Å and two broad peaks indicating the presence of cellulose in the RH feedstock. Ciolacu et al. [34] obtained similar broad peaks at $22.6^\circ 2\theta$ for cellulose, while Ju et al. [35] reported that bleach wood pulp produced a broad cellulose peak at $20.53^\circ 2\theta$. Cellulose in the feedstock decomposed upon heating to produce a broad peak in the XRD patterns of the biochars (Figure 2).

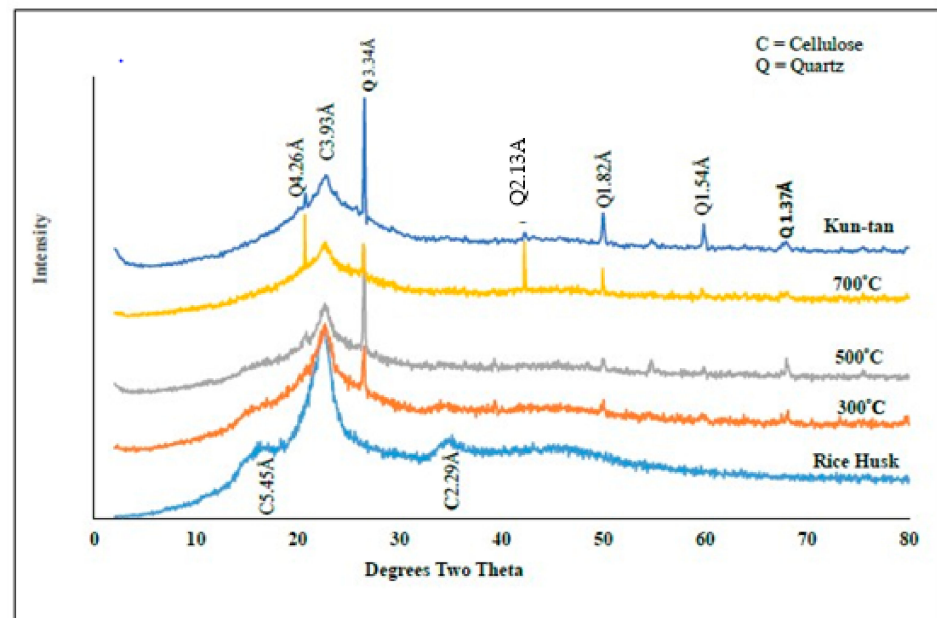


Figure 2. X-ray diffraction patterns of rice husk feedstock and rice husk biochar (RHB) pyrolyzed at 300 °C, 500 °C, and 700 °C and by Kun-tan.

The X-ray pattern of the RH feedstock did not reveal the presence of quartz; however, the XRD patterns of the biochars were dominated by quartz peaks. Hydrated amorphous silica is present in RH as biogenic opal [36], the only reported silicon phase found in plants [37–39]. Furthermore, rice is known to benefit from silicon nutrition [40], and the depletion of available silica in soils under intensive rice cultivation has been shown to reduce yield [41]. The XRD results showed that the hydrated amorphous Si in rice husks dehydrated and crystallized during pyrolysis to form quartz, regardless of pyrolysis temperature. The results suggest that quartz crystallinity increased with increasing pyrolysis temperature, because the 4.26 Å and 2.13 Å peaks of the 700 °C produced RHB that was more intense than the peaks for biochars produced at lower temperatures (Figure 2).

Hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$] and quartz were identified as the dominant crystalline minerals in both calcinated and raw BPR (Figure 3). The peaks corresponding to quartz and hydroxyapatite did not change in response to calcination temperature, indicating that the hydroxyapatite and quartz were stable up to at least 700 °C (Figure 3). Gilkes and Palmer [32] found structural changes upon calcination of phosphate ore in

samples dominated by millisite and crandallite, but there were no structural changes in ores dominated by apatite calcinated at 600 °C. Unlike the biochars, which varied considerably from the original feedstock, the XRD patterns of the calcinated BPR samples were similar to the XRD patterns of the phosphate ore.

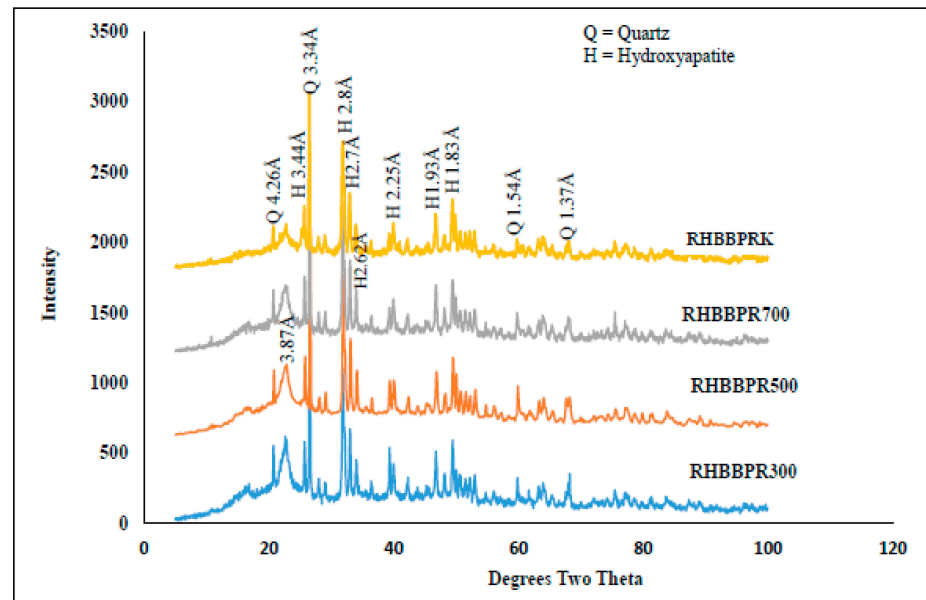


Figure 3. X-ray diffraction patterns of Burkina phosphate rock (BPR) and BPR calcinated at 300 °C, 500 °C, and 700 °C.

The RHB-BPR mixture showed X-ray patterns that were similar to those of the calcinated and non-calcinated BPR (Figure 3). The properties of RHB were masked by the crystallinity of the PR because neither the broad 3.93 Å cellulose peak nor the 2.13 Å quartz peak were visible (Figure 3).

3.2. Nitrogen, Hydrogen, and Sulfur Content of RHB, BPR, and RHB-BPR Mixtures

Table 1 shows that N, H, and S contents of RHB were similar to values reported for RH biochars in the literature [19,42]. Although the pyrolysis of RH significantly increased the N concentration from 0.39% in the feedstock to 0.54% in the 500 °C RHB, no overall trend was observed, because the N concentration was not related to pyrolysis temperature (Table 1). These results contrast with the findings of Hossain et al. [43], who reported a general decrease in N concentration of sludge biochar as a result of the volatilization of nitrogen during pyrolysis. However, the pyrolysis of RH significantly decreased H and S contents in the biochars (Table 1). Unlike the N content, H and S values showed a decreasing trend with increasing pyrolysis temperature among the laboratory-produced biochars. The H and S values obtained for RHBK were lower than those for the 500 °C produced biochar, but the H content of RHBK was higher than that of the 700 °C laboratory-produced RHB. The results could be a reflection of the variable nature of the pyrolysis temperature of the Kun-tan method. Jindo et al. [19] reported that the N and H content in RHB produced between 400 °C and 800 °C decreased with increasing pyrolysis temperature. Although we did not find this trend for N content, because the 500 °C biochar showed an increase in N concentration coupled with the variable temperature of the Kun-tan method, the decreasing trend was observed with H content.

Table 1. Selected chemical properties of rice husk (RH), RHB, BPR, and RHB-BPR mixture.

Materials	N %	H %	S %	pHw	Ash %	C %
RH feedstock	0.39d	4.97a	0.22a	6.20	19.59	35.07c
RHB 300 °C	0.48b	2.71a	0.26ab	6.38	39.79	40.36a
RHB 500 °C	0.54a	2.06c	0.08bc	6.64	46.55	34.62c
RHB 700 °C	0.43cd	1.82d	0.06bc	7.69	47.82	40.81a
RHBK	0.43c	2.05c	0.04c	6.53	43.89	37.99b
BPR RAW	BDL	0.34a	0.17a	6.40	NA	BDL
BPR 300 °C	BDL	0.23ab	0.12b	7.03	NA	BDL
BPR 500 °C	BDL	0.20b	0.08bc	6.48	NA	BDL
BPR 700 °C	BDL	0.20b	0.05c	6.37	NA	BDL
RHB-BPR 300 °C	0.01b	1.20a	0.05b	6.76	NA	16.17a
RHB-BPR 500 °C	0.02b	0.99ab	0.04b	7.07	NA	17.12a
RHB-BPR 700 °C	0.02b	0.85b	0.03b	7.26	NA	16.13a
RHB-BPRK	0.20a	0.99ab	0.73a	6.50	NA	15.44a

Different letters indicate significant differences ($p < 0.05$). BDL = below detectable limit. NA = not applicable.

Nitrogen concentration in the PR was below the detection limit. Phosphate rock is not known as a source of nitrogen, and some earlier work found N concentration in PR to be low or below detectable limits [44,45]. Hydrogen and S concentrations of the PR were low and showed a decreasing trend with increasing calcination temperature (Table 1). Hydrogen concentration of 0.34% recorded in the raw PR was significantly reduced to 0.20% in the 700 °C calcine. Sulfur content showed the same trend, significantly declining from 0.19% in the raw PR to 0.05% in the 700 °C calcine (Table 1). Dehydroxylation and volatilization may be the reasons for the decreasing trend with increasing calcination temperature. Dehydroxylation of goethite contained in PR has been reported by Gilkes and Palmer [32].

The elemental composition of the RHB-BPR mixtures did not follow any particular trend with respect to pyrolysis/calcination temperature. Nitrogen concentration significantly increased from 0.01% in the 300 °C mixture to 0.20% in the Kun-tan produced mixture, before declining and stabilizing at 0.02% for both the 500 °C and 700 °C mixtures (Table 1). Hydrogen concentration generally decreased with increasing pyrolysis/calcination temperature. Sulfur followed the same trend as N, increasing from 0.05% in the 300 °C mixture to 0.76% in the Kun-tan product (Table 1). The reasons for the increased concentrations of N and S in the RHB-BPRK mixtures are not understood.

X-ray fluorescence elemental analyses, reported on an oxide basis, showed that BPR was dominated by CaO, about 40%, P₂O₅ (29.8%), and SiO₂ (~20%). Fe and Al concentrations were low. Fe₂O₃ was ~2.5% and Al₂O₃ was 3.5% (Table 2). The low concentrations of aluminum and iron in the BPR ruled out crandallite and millisite as important components of BPR. The PR from the Kodjari deposit, Burkina Faso (BPR), has been reported to mainly consist of fluorapatite (Ca₅(PO₄)₃F) and quartz (SiO₂), with a P₂O₅ content of 34.1% or 14.9% P [46]. However, no evidence of fluorapatite was found in the sample used in this research. The P₂O₅ content found in the BPR was higher than the 25% stated on the product by the manufacturer, but lower than the 34.1% reported by Nakamura et al. [46]. Similarly, the CaO of 40% and the 30% P₂O₅ content of the Burkina PR were higher than the 23% and 11% reported by Hammond et al. [31]. The Al₂O₃ + Fe₂O₃ content of 5.7% was similar to other findings in the literature [31,47]. These variations in reported elemental composition of BPR suggest that different samples of the ore may have somewhat different compositions, but overall, apatite is the dominant mineral phase in BPR.

Table 2. Chemical composition of BPR determined by X-ray fluorescence spectrometry.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	TiO ₂	BaO	SrO	Mn ₂ O ₃	Basis
(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	
20	3.56	2.13	0.19	40.1	0.32	0.28	0.15	29.8	0.22	0.07	0.17	0.05	LOI-free
19.4	3.46	2.06	0.18	38.9	0.31	0.27	0.15	28.9	0.21	0.07	0.16	0.05	Oven-dry

3.3. Carbon and Ash

The carbon concentration in the biochars ranged from 34% in the biochar produced at 500 °C to 40.8% in the biochars produced at 700 °C (Table 1). The lowest C concentration occurred in the 500 °C biochar rather than the 300 °C biochar. It appears that pyrolysis temperature of RHB does not produce a regular pattern in terms of carbon concentration. The irregular pattern and the values obtained in this study are similar to those reported for RHB biochars by Jindo et al. [19]. The ash content of the biochars showed a regular pattern, increasing with increasing pyrolysis temperature (Table 1).

3.4. Effect of Temperature on pH of RHB, BPR, and RHB-BPR Mixture

Temperature effects on the pH of RHB as presented in Table 1 reveal that the pH of RHB increases with increasing pyrolysis temperature. The pH increased from 6.20 in the feedstock to 7.69 in the 700 °C RHB, an increase of 1.5 pH units. Jindo et al. [19] found that the pH (1:10 biochar:water ratio) of RHB pyrolyzed between 400 °C and 800 °C and increased from 6.84 to 9.62. Although the pH of biochar is known to increase with increasing pyrolysis temperature [18,20], others have reported that pH values that show an initial dip for low-temperature biochars derived from biosolids and cattle manure before increasing to values >10 [33,43]. Biochar pH reflects both the ash content and composition of the feedstock as well as the pyrolysis temperature [20].

The pH of BPR did not follow the trend observed with the RHB (Table 1). Low-temperature calcination at 300 °C caused an initial increase in pH from 6.40 to 7.03, followed by a decrease in pH to 6.37 in the 700 °C calcined BPR. These results indicate that low-temperature calcination increased pH while high-temperature calcination decreased pH, albeit slightly. Although the reasons for the pH changes are not entirely understood, the ease of dissolution of constituent minerals like calcite in water may account for this pattern. High-temperature calcines (>750 °C) are reported to show slower rates of dissolution in citric acid and ammonium citrate, whereas low-temperature calcines (<350 °C) show a faster rate of dissolution [31]. While dissolution rate was not the focus of this study, it is possible a similar dissolution rate in water as found by Gilkes and Palmer [32] may explain the pH pattern.

3.5. FA-Extractable P in RHB, BPR, and RHB-BPR Mixture

The available (i.e., formic acid-extractable) P concentrations of the RHB300, RHB500, and RHBK were not significantly different from the available P content of RH feedstock; however, available P content of RHB700 was significantly different from the feedstock and the other biochars. Available P content increased from 221 mg kg⁻¹ P in the feedstock to 707 mg kg⁻¹ in the 700 °C biochar (Figure 4). At 700 °C, the available P content of the RHB was 219% more than the feedstock. In a study with biochars produced from dairy manure-wood mixture and biosolid-wood mixture, [33] they also reported increases in formic acid-extractable P of the biochars with increasing pyrolysis temperature. Amending with high-temperature RHB could therefore be a low-cost soil management option that could be used by small-scale rice farmers of the interior savanna of Ghana to enhance the P content of the lowland soils of northern Ghana and, thereby, increase the productivity of their farms.

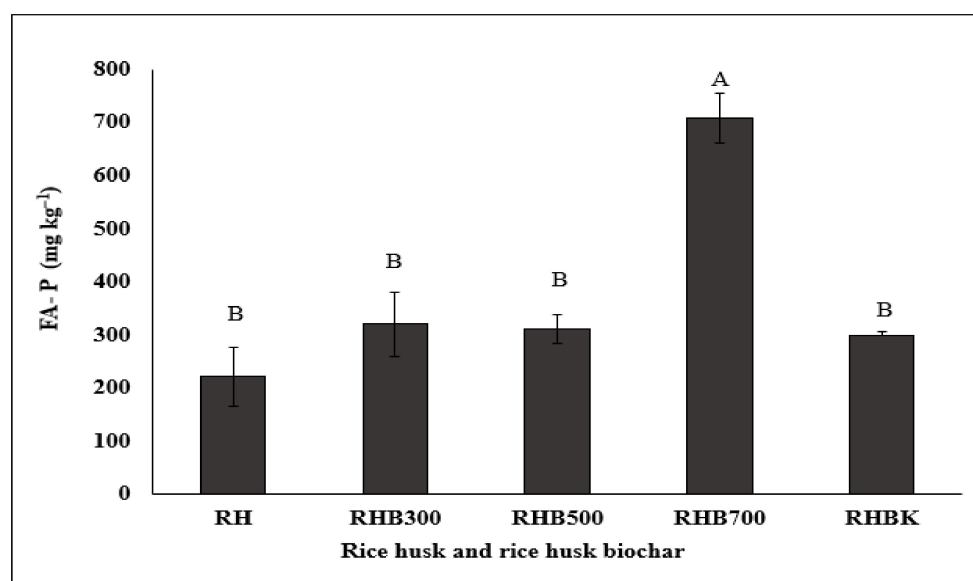


Figure 4. “Available” (i.e., formic acid-extractable) phosphorous (P) content of RH and RHB at different pyrolysis temperatures. Error bars are standard errors. Letters on top of error bars show significant difference at $p \leq 0.05$.

Available P content in the PR decreased with increasing calcination temperature, ruling out thermal calcination as a viable option for solubilizing BPR (Figure 5). Actually, calcination of BPR reduced available P content in the 300 °C, 500 °C, and 700 °C calcines by 12%, 19%, and 22%, respectively. This finding is in contrast with the findings of Nakamura (2018), who reported an initial increase in citric acid-soluble P at 300 °C to 400 °C before decreasing at higher temperatures. Defluorination is the main process by which thermal treatment of PR results in increased available P [24]. Perhaps the absence of fluorapatite in the PR sample used hindered the process. Further studies are recommended to understand why calcination of hydroxyapatite-dominated PR resulted in decreased P content. Gilkes and Palmer [32] did not observe any marked increase in citric acid-extractable P as a result of calcination of appetite-dominated RP ore. However, they observed a slow citric acid dissolution of high-temperature calcines, which they attributed to reduced specific surface area of the high-temperature calcines. It is possible that FA-induced dissolution of higher temperature calcines was slow because of reduced specific surface area. The FA-extractable P content of the RHB-BPR mixture followed the same trend as observed among the BPR calcines, although the changes in available P were not statistically significant. Available P decreased with increasing temperature among the RHB-BPR mixtures (Figure 6).

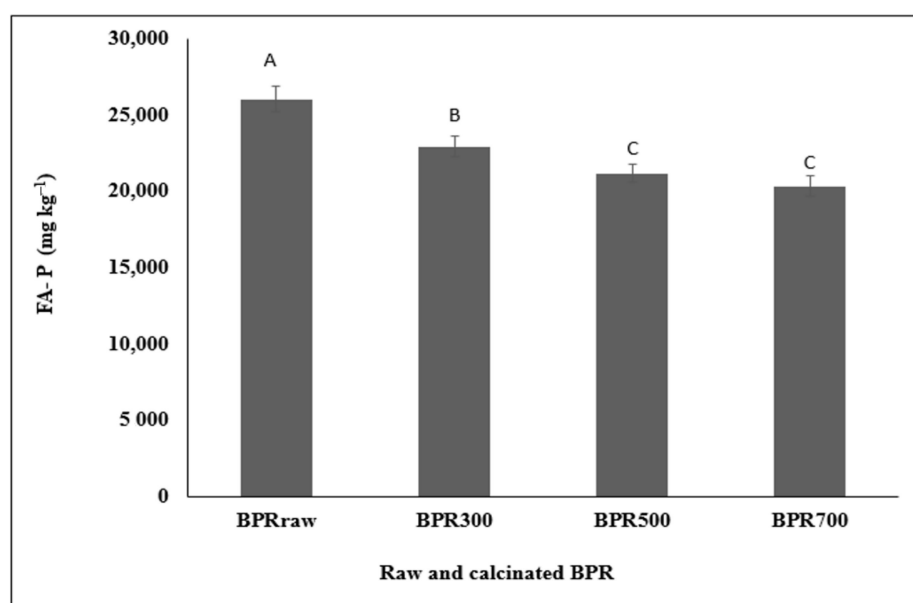


Figure 5. “Available” (i.e., formic acid-extractable) P content of raw BPR and calcinated BPR at different calcination temperatures. Error bars are standard errors. Letters on top of the error bars show significant difference at $p \leq 0.05$.

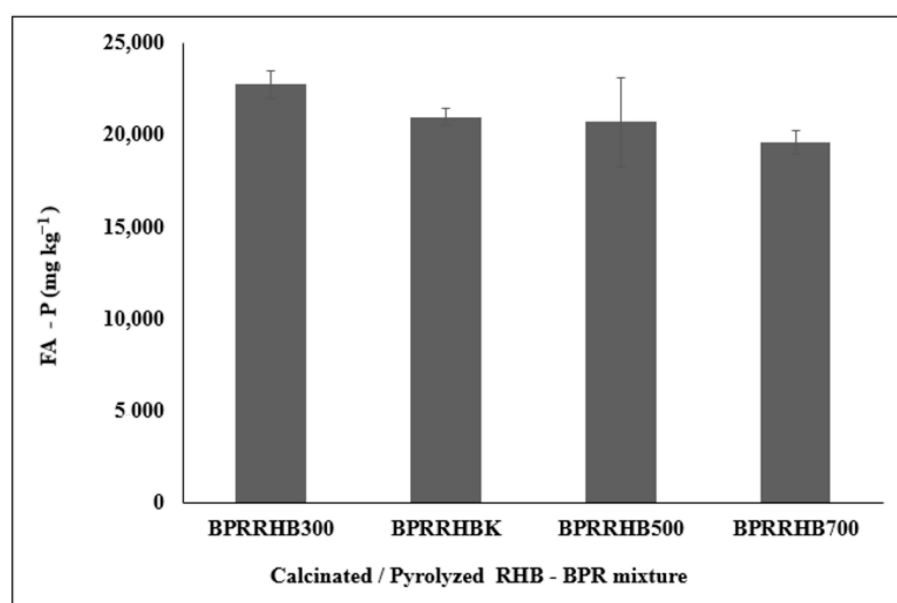


Figure 6. “Available” (i.e., formic acid-extractable) P content of RHB-BPR mixture at different pyrolysis/calcination temperatures showing no significant difference at $p \leq 0.05$. Error bars are standard errors.

4. Conclusions

The study showed that pyrolysis temperature and calcination temperature significantly impact the chemical properties of RHB and BPR. Formic acid-extractable P, pH, and ash content of the biochars increased with increasing pyrolysis temperature, whereas the FA-extractable P content of the BPR decreased with increasing calcination temperature. High-temperature RHB could become an important source of plant-available P for small-scale rice farmers in the interior savanna of Ghana. Although the quantity of RHB required to meet plant P requirements was not the focus of this study, the long-term application of RHB could help mitigate the P deficiency often cited as the most limiting factor to rice

production. However, calcination does not appear to be a viable option for increasing the solubility of P in BPR, at least within the temperature ranges considered in this study.

The XRD analysis revealed hydroxyapatite and quartz as the principal constituents of Burkina PR. Aluminum and iron concentrations of BPR were found to be low, ruling out crandallite and millisite as important components of BPR. Mineralogical properties of RHB were affected by pyrolysis temperature, while the mineralogical properties of BPR were unaffected by calcination temperature. Biogenic opal in the rice husk dehydrated during pyrolysis to produce quartz-rich RHB, which is an added advantage because of the importance of silica in rice nutrition. Cellulose contained in RH and RHB produced a broad XRD peak centered near 3.93Å. The XRD patterns of BPR ore and calcinated BPR were similar irrespective of calcination temperature, showing that hydroxyapatite-dominated PR remains stable when heated to at least 700 °C. Calcines of RHB-BPR mixture exhibited similar mineralogical properties as the PR and the mineralogy of the mixture remain unchanged irrespective of pyrolysis/calcination temperature.

Thus, our overall conclusions are that rice husk biochar could be used as an additional soil amendment to increase available P in the lowland rice cropping systems of Ghana. Burkina PR could also be used directly to supply P for rice cultivation as well; however, BPR should neither be calcinated nor co-pyrolyzed with RH as it is found in this study to reduce the availability of P from BPR.

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