Effect of process conditions on properties of biochar from agricultural residues

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Abstract. In northern Thailand, there are a great amount of agricultural residues generated after the harvest, most of which are burned as a means of disposal, affecting the soil for agriculture, wild animals, as well as causing air pollution. One of the solutions that may be beneficial in terms of carbon credit is to turn these agricultural residues into biochar using slow pyrolysis. Biochar is widely accepted biologically derived matter with the ability to contain carbon, large amount of nutrients, adding biodiversity in soils. The attribute of biochar is varied depending on its production process. This research aims to study biochar production conditions and possible attributes with slow pyrolysis process under 100 ml/min nitrogen condition. Two types of agricultural residues including rice husk and corn cob were used, at the process temperature of 300-700 °C. The results indicated that when the temperature was increased, the produced biochar decreased, but different amounts of carbon, electrical conductivity, amounts of inorganic minerals (N, P, K, Mg, Ca, Fe), and alkalinity increased. This enabled the produced biochar to add more carbon to the soil when used, reduce acidity or alkalinity, as well as help the soil to contain more water and other required nutrients for plants better and become a home to microbe. More air ventilation was allowed in the soil, improving its quality.  

1. Introduction  
Biochar is a porous material that contains a high amount of carbon which could be directly used and could be naturally dissolved [1]. Biochar could be produced from biomass such as agricultural residues and some leftover slivers [2] through slow pyrolysis at 300-800 °C [2, 3] under vacuum or nitrogen condition [4]. Its attributes that could be used to improve soil quality are affected by many factors such as temperature, time of heat, and the type of biomass [5].  

Currently, there are many studies on biochar production and its many uses. Production conditions such as temperature during the slow pyrolysis could affect the physical and chemical structures of the biochar such as the change in volume [3], carbon [6], acidity [7], and ion exchange ability, surface and holes [8, 9]. From these studies, it was revealed that each attribute is dependent on the composition of biomass [10]. Each biomass has different chemical reaction [11] when receiving heat at different amount of time such as corn cob [7], bamboo [12], rice husk and rice straw [13].
Studies on the effect of temperature on biochar properties such as pH and electrical conductivity (EC), CEC, BET, and SEM of biochar. It was found that pH was increasing with temperature. In the range between 300-800 °C, pH of most biochar from corncob and rice husk were around 8-10 which was suitable for medium to strong acid soil. EC of biochar were around 0-1 which was suitable for improving soil with strong alkalinity. To the authors’ knowledge, there remains a lack of study on biochar that may be applied to low-acidic to low-to-medium or weak alkalinity soil [1, 9, 10, 13-15].

Biochar could be produced from various reactors such as fixed bed, fluidized bed, and microwave reactors. Each reactor has different functionality. However, fixed bed reactors are still widely accepted and easy for slow pyrolysis, different from other reactors as they are commonly used for fast pyrolysis instead [16-18].

The objective of this work were to study the production factors affecting the attribute of produced biochar as well as to study physical and chemical changes such as its volume, acidity, electrical conductivity, number of elements, surface, and holes in order to find the most appropriate attributes suitable for improving soil.

2. Materials and methods

2.1 Biochar feedstocks
There were two types of materials used to convert into biochar. They were rice husk (RH) and corn cob (CC). These materials were obtained locally from Chiang Mai in Northern Thailand.

2.2 Production of biochar
Before pyrolysis, the raw materials must have their moisture reduced to lower than 10% of their weight [19]. In each experiment, 20 g of the biomass sample was loaded into the test cup, then brought into the operational fixed-bed reactor. Slow pyrolysis was done under nitrogen (N2) condition with 100 ml/min flow rate. The temperature used in the experiment was 300, 400, 500, 600, and 700 °C with a heating rate of 10 °C/min [20]. Once reaching the set value, the temperature was stabilized in the set time before reducing the temperature under nitrogen condition. During the cooling process, physical and chemical changes were expected to be ongoing.

2.3 Characterization of biochar
The amount of biochar could be determined from overall mass balance where Wf and Ws were obtained from dry mass of biochar products and dry mass of biomass used in the experiment [21].

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\text{Biochar yield (\%) } = \left( \frac{W_f}{W_o} \right) \times 100
\]

The moisture content of the biochar was analyzed according to the ASTM D1762-84 standard at 105 °C temperature for 2 h [19], then pH value was measured using the analysis according to DIN ISO 10390 with 1:5 (W:V) biochar to 0.01 M CaCl2-solution, 60 min shaking, measuring directly in the suspension and EC analysis by DIN ISO 11265, adding 1:10 (W:V) H2O to the sample, shaking for 60 min, followed by filtration of the solution. (According to EBC standard). Morphology study of biochar was done using a scanning electron microscope (SEM) with 15 kV of electron beam where they would react with the beam and biomass sample with 10 μm or 2,000 x microscope and using energy-dispersive X-ray spectroscopy (EDX) with random scan on the surface of the biochar, which would result in the micron level.

3. Results and discussions

3.1 Mass yield of pyrolysis product
The amount of biochar produced was dependent on the pyrolysis process. High temperature was used during pyrolysis, resulting in decreasing the amount of produced biochar, as shown in Table 1. At the temperature between 300-400 °C, the biochar produced from rice husk and corn cob were quickly decreased from 54.81% to 46.95% and 36.49% to 32.91%, respectively. In this temperature range,
cellulose and hemicellulose were dissolved. When temperature higher than 400 °C was used, the produced biochar from rice husk was decreased by about 2%, similar to the biochar produced from corn cob. They were continuously dissolved exponentially, resulting in continuous reduction in the produced biochar. The temperature in this range caused cellulose and lignin to dissolve, as shown in Figure 1. [6], and they showed complex and different structures. Therefore, the amount of the produced biochar would depend on the reaction temperature that caused hemicellulose, cellulose, and lignin to decompose. The amount of the three components could indicate the temperature. If the amount of hemicellulose and cellulose was low, they would decompose at 300-400 °C. They would decompose less in higher temperature like rice husk. If the amount of cellulose and lignin was high, they would decompose in higher temperature of 400-500 °C and the produced biochar would continuously decrease with increasing temperature. Biomass with different proportion of lignocellulosic components would decompose differently, causing the differences in the amount of the produced biochar.

Table 1. Comparison of biochemical properties at different temperatures in the pyrolysis process

| Feedstock | Temperature (°C) | Yield (%) | Water content (% wt) | pH | EC (ds m⁻¹) |
|-----------|------------------|-----------|----------------------|----|-------------|
| RH        | -                | -         | 2.51                 | 5.81 | 2.44 |
|           | 300              | 54.81     | 0.379                | 5.82 | 2.57 |
|           | 400              | 46.91     | 0.54                 | 6.14 | 2.58 |
|           | 500              | 46.18     | 0.346                | 8.97 | 2.50 |
|           | 600              | 44.19     | 0.307                | 9.61 | 2.60 |
|           | 700              | 44.01     | 0.308                | 10.79 | 2.62 |
| CC        | -                | -         | 5.30                 | 5.18 | 0.15 |
|           | 300              | 36.49     | 3.785                | 5.38 | 0.16 |
|           | 400              | 32.91     | 3.416                | 6.14 | 0.26 |
|           | 500              | 30.23     | 2.894                | 7.74 | 0.27 |
|           | 600              | 24.95     | 2.381                | 8.18 | 0.27 |
|           | 700              | 22.90     | 2.208                | 10.15 | 0.37 |

3.2 pH and EC
Higher temperature in the pyrolysis process caused the pH to increased [1] as shown in Figure 2. pH was correlated to volatile matter and O/C ratio that related organic function groups of material which value were different between each material composition [22]. When increasing temperature, total acidity of the functional groups increased while the amount of functional groups decreased [15]. At 300-700 °C, it was found that the pH in both types of biomass char were different at 5.82 to 10.79 and 5.39 to 10.15, respectively. At 300-400 °C, the biochar would become acidic with the pH between 5.38 to 6.14, which was suitable to be nutrients for microorganisms in the soil. At a temperature higher than 400-700 °C, the pH was shown to be alkalinity, which can adversely affect microorganisms in the soil when used. It can also change the absorption of required nutrients, affecting the growth of plants.

Electrical conductivity (EC) is an important factor that indicated saltiness when used to improve soils. Increasing temperature in pyrolysis also increased the electrical conductivity, as shown in Figure 3 [19]. Both types of biochar appeared to have different electrical conductivity. The biochar produced from rice husk had higher conductivity than that from corn cob at 2.57 ds m⁻¹ to 2.62 ds m⁻¹ and 0.16 ds m⁻¹ to 0.37 ds m⁻¹, respectively. The biochar from rice husk had higher electrical conductivity than that from corn cob by about 10 times. Therefore, rice husk (RH) was suitable for improving soils with weak alkalinity, while corn cob (CC) was suitable for improving soils with strong alkalinity.

3.3 SEM analysis
From the morphology of the biochar at 2,000x, it was found that increase in temperature also increased holes found in the biochar, as shown in Figure 4, [23]. Holes in the biochar from rice husk and corn cob were different for each temperature. At low temperatures, the holes were small, while increasing
temperature appeared to increase the size of the holes with uniform dispersion [15]. Holes in the biochar would help absorbing water or other nutrients in soils.

3.4 Energy dispersive X-ray spectrometry

In the analysis of elements in the biochar shown in Table 2, it was found that temperature affected the changes in elements. Increasing temperature increased the amount of C, Mg, N, O, P, and K while decreased the amount of Fe and Si. When the temperature was increased, the number of elements in rice husk and corn cob were different. In corn cob, the amount of carbon was high, in the form of CaCO$_3$ while in rice husk, the amount of silicon and oxygen were high, in the form of SiO$_2$, while N was only found in rice husk and Si was also high while they could not be found in corn cob.

![Figure 1. Effect of pyrolysis temperature on the biochar yield.](image1)

![Figure 2. Comparison of the biochar pH](image2)

![Figure 3. The difference of biochar feedstock](image3)
Figure 4. SEM image of biochar from rice husk (a) RH, (b) RH300, (c) RH400, (d) RH500, (e) RH600 and (f) RH700

Figure 5. SEM image of biochar from corn cob (g) CC, (h) CC400, (i) CC500, (j) CC600 and (k) CC700

Table 2. Elements in the biochar with EDX

| Sample | Element composition (% wt) |
|--------|---------------------------|
|        | C  | N  | O  | P  | K  | Mg | Ca  | Fe  | Si  |
| Feedstock |    |    |    |    |    |    |     |     |     |
| RH     | 18.97 | 12.77 | 55.43 | - | 0.09 | - | 0.03 | 0.27 | 12.25 |
| CC     | 55.46 | - | 44.54 | - | - | - | - | - | - |
| Biochar |    |    |    |    |    |    |     |     |     |
| RH300  | 14.91 | 6.69 | 76.38 | 0.84 | - | 0.02 | - | 0.14 | - |
| RH400  | 11.62 | 10.76 | 64.62 | 0.1 | 0.4 | - | 0.2 | - | 11.67 |
| RH500  | 19.3 | 6.69 | 62.51 | 0.03 | 0.22 | 0.07 | - | - | 10.76 |
| RH600  | 13.62 | 7.22 | 77.99 | 0.31 | 0.38 | 0.31 | - | - | - |
| RH700  | 22.01 | 7.42 | 69.68 | 0.34 | 0.31 | - | - | - | - |
| CC400  | 38.37 | - | 13.98 | 0.1 | 44.89 | - | - | - | - |
| CC500  | 89.85 | - | 8.85 | 0.13 | 0.59 | - | 0.19 | 0.03 | - |
| CC600  | 80.93 | - | 11.31 | 0.15 | 6.45 | 0.02 | - | - | 0.27 |
| CC700  | 66.73 | 28.46 | 3.95 | 0.04 | 0.42 | 0.08 | 0.01 | 0.07 | - |

4. Conclusions

Reaction temperature appeared to affect the attributes of the biochar produced. It was found that increasing temperature during slow pyrolysis increased pH and alkalinity. The type of biomass affected the amount of EC, while SEM showed larger holes and EDX caused changes in elements differently from the amount of the produced biochar and decrement of moisture. Biochar from rice husk had higher EC than corn cob around 10 times. It was suitable for improving soils with weak alkalinity while corn cob was suitable for improving soils with strong alkalinity.
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