Study on the Properties of Rice Straw Biochar Caused by the Soil Nitrogen Application Rate Difference

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Abstract: The agricultural straw burning is one of important environmental concern, and how to rationally utilize straw resources is important for sustainable development. Due to high carbon content and strong stability, straw biochar by pyrolysis has become a hotspot study in multidisciplinary fields. This study focused on biochar properties and soil type and carried out in the same experimental plot with different nitrogen fertilizer application rates. There were still differences in straw charcoal and in the future, the study on the interaction between biochar properties and soil shall be continued to improve the carbon fixation and emission reduction

1.The Literature Review

1.1.Introduction

The CO_2 and water in the atmosphere, which can be produced under light conditions, can provide essential nutrients for plants. Most of the plant carbohydrates are found in straw, and we harvest only food and seeds. Therefore, the straw is a waste of resources. Then, the straw biochar can be obtained after a certain temperature pyrolysis without oxygen or restrictive oxygen supply conditions.

1.1.1 Introduction to straw

Straw is the general term for the stem leaves (fringe) of mature crops. It usually refers to the remaining portion of wheat, rice, corn, potatoes, rapeseed, cotton, sugarcane, and other crops (usually coarse grains) after harvest. More than half of the product of crop photosynthesis exist in straw, which has ample organic matters like nitrogen, phosphorus, potassium, calcium, and magnesium, making it a versatile and renewable biological resource.

In 2021, The annual output of straw reached 700 million tons in China. Agricultural development underpins civilization and progress. After entering the agricultural society, people need to deal with the urgent problems from agricultural residues - straw. Considerable amount of residual straws were left after the farmland harvest. In ancient times, people invented "slash-and-burn" farming method, which burn residual straw and return its nutrients to agricultural soil. This method is nevertheless not suitable for modern society, for the greenhouse gases from straw burning increased carbon emissions, destroyed the ozone layer, and polluted the atmosphere, water and soil environment. This will lead to global warming, an environmental concern in the world today, and the closely related carbon cycle mechanism has become a research hotspot in the scientific field(Wang et al, 2017)[18].

1.1.2 Introduction to Biochar

Biochar is an insoluble, stable and highly aromatic solid matter produced by slow pyrolysis of biological residues at high temperature (usually<700 ℃) in the absence of oxygen (Singh et al., 2010 [16]; Li et al., 2011[8]; Titirici et al., 2007[17]). Biochar contains stable carbon elements, in which carbon consists aromatic hydrocarbon, simple carbon or carbon with graphite-like structure (Chen et al., 2013[2]). The surface structural characteristic defines its high chemical and biological stability. Biochar, featuring abundant surface microporous structure, has a large specific surface area, strong adsorption capacity, and high affinity for heavy metals, inorganic substances, and organic pollutants. It can adsorb them and affect their migration in soil, thus reducing their bioavailability in soil, or decreasing their soil loss. Biochar is mainly used as a soil additive to enhance soil fertility and increase the soil carbon sink (Lehmann et al., 2009[7]), and can provide long-term nutrient supplement for crop growth (Oladele, 2019[12]), and improve farmland soil improvement, fermentation and regulation. And research shows an effective and timely soil management strategy needs to be urgently developed not only to improve crop yield and quality, but also to enhance soil fertility (Oladele et al., 2018[13]).

1.2.Benefit of using biochar

The mechanisms of biochar action in slowing down global climate change and improving soil productivity have attracted much attention (Lehmann, 2007[6]). Studies have

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shown that biochar has low carbon emissions during cogeneration and can reduce greenhouse gas production and emissions by improving the physical and chemical properties of the soil (Zhang, 2014[20]), and can also reduce Carbon dioxide (CO2) emissions in some areas (Qi et al., 2018[14]). Moreover, biochar has the advantages of retaining water, retaining nutrients, improving soil environmental quality, and being conducive to microbial reproduction (Yu et al., 2018[19]). It has strong adsorption, can adsorb soil ions, is conducive to reducing the loss of elements, improves grain output, promotes grain growth (Khan et al., 2013[5]), and has substantial economic benefits. Also, the biochar treatment of straw is conducive to the protection of water resources because the water body discarded straw will pollute the water body. Failure to discard one ton of straw from the water body is equivalent to dropping one bag to half a bag of nitrogen, phosphorus, and potassium compound fertilizer into the water body. In addition, studies have shown that after applying straw biochar to soil with poor fertility, ryegrass production has increased by 7%, 27%, and 53% compared with control, respectively (Zhu et al., 2022[21]). The ash in the biochar contains a certain amount of mineral nutrients, and sludge and livestock manure have a higher content than wood (Sue et al., 2022[15]), straw and shell biochar, which could supplement some nutrient supply of poor soil and sandy soil.

1.3.The change of biochar properties with the pyrolysis temperature

Many experiments have proved that straw biochar will show different structural characteristics and properties at different preparation temperatures. There are broadly literature shows that: 1, the preparation method of biochar is different, and its properties are very different .2, the carbonization yield of biochar gradually decreases with increasing temperature. 3, wheat straw thermal weight analysis diagram shows: a 100~200℃ biomass sample with no apparent loss, the stage is the occurrence of the wheat straw internal tissue depolymerization and a slow process of "glass transition", the temperature continues to increase the pyrolysis of wheat straw, when the temperature rises to 350℃, the sample loss rate, the sample loss 33.73%, 500℃ after fixed carbon combustion primary end, the sample loss rate gradually flat. 4, With the increase of carbonization temperature, the content of carbon element increases, the content of oxygen and hydrogen element decreases, and the biochar gradually becomes "carbon-rich" particles; With the increase of carbonization temperature, the polarity of biochar decreases (Liu et al., 2021[11]), the aromatic and hydrophobic properties are significantly enhanced, and the surface unstructured components decrease(Chang et al., 2017[1]).

Also, the key Laboratory of Organic Pollution Process and Control of Zhejiang Province also used rice straw as raw material to prepare straw biological carbon at different temperatures (100℃~700℃). The experiment through TG-DTG thermal weight analysis, CHNO elements, FTIR, BET-N2 than the surface and aperture distribution of the composition and structure of biological carbon, found that rice straw biological carbon contains the rich organic carbon component and the inorganic mineral component, with the rise of cracking temperature, biological carbon in organic carbon content gradually increased, weakened polarity, aromatic, and the relative content of an inorganic mineral component is increasing (Chen et al., 2013[4]).

1.4.The change of biochar properties with species of crops

The biochar industry often studies and discusses the difference in the biological carbon fired by different types of straw. Many works of literature show that: 1, the pyrolysis temperature largely determines the properties of biochar preparation. With the increase of preparation temperature, the nutrient elements are enriched, and the biochar alkalinity becomes higher; rice straw carbon has high alkalinity, ash, total potassium, and surface oxygen-containing functional components, while corn stover carbon is rich in nitrogen and phosphorus components. 2, Two kinds of straw biochar can improve soil acidity and increase soil organic carbon bank. Adding rice straw carbon increased the level of quick soil potassium. In contrast, corn stover carbon mainly increases the content of quick phosphorus. 3, both types of straw biochar can increase soil microbial biomass carbon and phospholipid fatty acid content. The change of soil microbial community structure by rice straw carbon is more significant than that of corn stover carbon(Li et al., 2015[9]).

Also, Nanjing Agricultural University has researched the adsorption effect of Pb ~ (2 +) and Cd ~ (2 +) in different crops. The study shows that among the three kinds of straw carbon prepared by 450℃ oxygen-limiting thermal cracking, wheat and rice straw carbon can absorb more Pb 2 + and Cd 2 + with a higher adsorption rate. Also, the adsorption amount of corn stover carbon is relatively small, and the adsorption rate is relatively low. This may be related to the higher inorganic mineral components such as carbonate, phosphate, and silica and the higher amount of cation exchange. Corn stover carbon has a loose structure, good pore structure, a large specific surface area, and contains more oxygen-containing functional groups, mainly through surface adsorption and functional group complexation adsorption of metal ions(Li et al., 2015[10]).

1.5.Conclusion

Currently, most of the existing research data are focused on the change of biochar properties with the pyrolysis temperature and crop species, some are looking for the highest efficiency of biochar preparation at which temperature and which crop preparation is better. Some scholars also focus on the effect of different kinds of straw on the land during fertilization. They are all meaningful research and got much eminent research production. However, biochar still has many possible development directions(Chen et al., 2013[4]), and there are still research gaps in this area. One of those research gaps is to study the difference between the same kind of straw with difference in fertilization. Therefore, this study explored the possible differences in identical crops grown in different environment. This study aims to identify the optimal soil fertility conditions through the property analysis of biochar and thus guide fertilization.

2.Materials and Methods

2.1.Research Materials

The experimental plot is located in Shanghai, near the lower reaches of the Yangtze River and belongs to the northern subtropical tropical monsoon climate. The annual average temperature reaches about 16 ℃, and the annual average precipitation is about 1200 mm. About 60% of the rainfall is concentrated in the flood season from May to September. The soil pH (soil water ratio 1:5) is about 6.63, a conductivity of 500 uS cm^{-1}, and a bulk density of 1.4g cm^{-3}. The area of each experimental community is 80 m^2. The nitrogen fertilizer dosage in the rice season was applied in a ratio of 5:3:2 for base fertilizer, tiller fertilizer, and earing fertilizer; All phosphate fertilizers were basal applications, and the dosage was 100 kg hm^{-2} of Phosphorus pentoxide; The ratio of base fertilizer to earing fertilizer reached 1:14, and the amount of potassium fertilizer was 225 kg hm^{-2} of Potassium oxide.

Two treatments were set up based on converting the soil nitrogen application rate to pure nitrogen of 100 and 300 kg hm^{-2}. There was only a difference in nitrogen application rate during the rice season among different treatments, and the application time of N fertilizer, PK fertilization, and other management measures stayed the same. Conventional rice was used as the experimental material and transplanted in June. After the rice was harvested in late October, rice straw was collected.

Named the straw with soil nitrogen application rate to pure nitrogen of 100 kg hm^{-2}, Straw A. Named the straw with soil nitrogen application rate to pure nitrogen of 300 kg hm^{-2}, Straw B.

2.2.Research Methods

The stalks of rice straw were selected and cut into 2~3cm segments. They were naturally air dried at room temperature. The straw biochar was prepared by low oxygen temperature rising carbonization method and programmed temperature control carbonization furnace. The equipment has simple structure and good sealing performance. The specific method is as below: Place the dried rice straw into a 200 mL crucible, put it in the reaction chamber, close the furnace door, and open the heating program and temperature control heating program. Set the pyrolysis temperature to 300 ℃, 500 ℃, and 700 ℃, respectively, heat up in a nitrogen atmosphere, reach the pyrolysis temperature, carbonize for 2 hours, and naturally cool it to room temperature. Repeat the preparation three times under each treatment temperature condition. Crush the obtained carbonization product and pass it through a 20 mesh sieve for testing. Weigh the sample and put it into a plastic bottle. Add ultrapure water in a water and straw proportion of 20:1, with a water and straw carbon proportion of 50:1. Place the plastic bottle in a shaker and oscillate for 30 minutes at a constant temperature of 25 ℃. Utilize a pH meter to measure the pH value separately. After grinding and sieving the air dried soil sample to 100 meshes, it determined the content of total carbon, total nitrogen, and total hydrogen with an element analyzer (Vario EL Cube, Elemental, Germany), and the degree of aromatization was calculated.

3.Results

3.1.Biochar pH

The pH value changes of Biochar are indicated by Figure 1, which provides the detail comparison experimental results to demonstrate the impacts of pyrolysis temperature on biochar pH. The pH value of straw biochar from pyrolysis of straw A and straw B increased with carbonization temperature. When the pyrolysis temperature is 300 ℃, the pH change of biochar is neutral; When the pyrolysis temperature increases from 300 ℃ to 500 ℃, the pH sharply increases. As the pyrolysis temperature constantly rises, the straw charcoal becomes alkaline or even strongly alkaline.

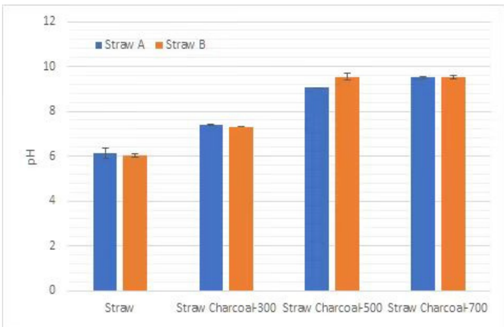

Figure 1 Biochar pH changes with pyrolysis temperature

3.2.Biochar carbon and nitrogen content

The carbon and nitrogen content of biochar is shown in Figure 2 and Figure 3 with rice straw ranges from 44.8% to 45.5%. The corresponding biochar increased with the pyrolysis temperature rise. From experimental data, the carbon content ranged from 67.6% to 81.6% and the nitrogen content of Biochar is about 0.8% and 1.3%. The corresponding biochar increased significantly with the pyrolysis temperature rise, and carbon and nitrogen content. Straw A has a higher nitrogen content in biochar prepared by pyrolysis (500 and 700 ℃) compared with straw B.

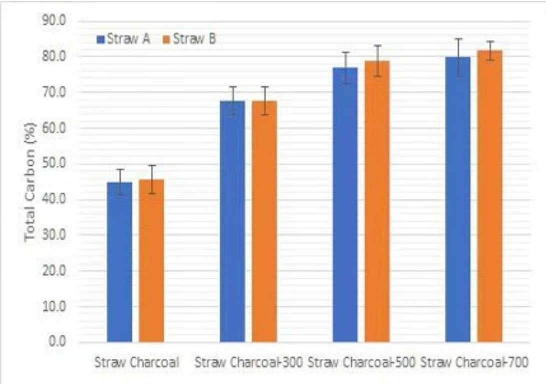

Figure 2 The carbon content changes of Biochar

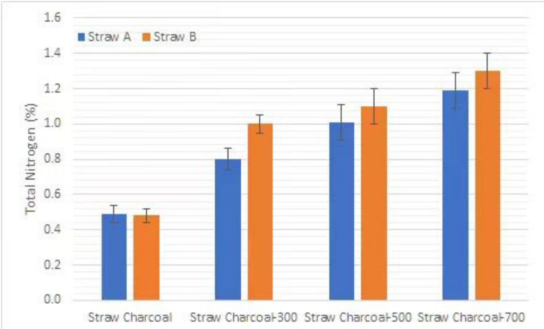

Figure 3 The total Nitrogen changes of Biochar

3.3.Biochar aromatization

Organic compounds containing benzene rings in molecules are called aromatic compounds. They usually refer to hydrocarbons with benzene ring structures in their molecules, which are a closed chain class. Aromaticity refers to: (1) Planar or nearly planar circular structure; (2) Bond length tends to average; (3) A high C/H ratio; (4) Aromatic rings of aromatic compounds are difficult to oxidize and add, but prone to electrophilic substitution; (5) Some special spectral characteristics, such as the chemical shift of the hydrogen outside the aromatic ring is in the low field of the NMR spectrum, while the hydrogen inside the ring is in the high field. Most aromatic compounds contain one or more aromatic rings (or aromatic nuclei). The pyrolysis temperature significantly influences aromatization of biochar, as the preparation temperature and the specific surface area of biochar increase, the carbon content rises, the oxygen content and the O/C decrease, the hydrophilicity and polarity of Biochar and the affinity for water molecules decreases, and the adsorption of hydrophobic pollutants improves.

The H/C mole of biochar was indicated by Figure 4, and the H/C mole ratio of rice straw was about 1.6. The corresponding biochar decreased with the pyrolysis temperature rise dramatically to 0.8 ~ 0.2, but same trend for Straw A and Straw B. The O/C mole of biochar was indicated by Figure 5, and the O/C mole ratio of rice straw was about 0.01. The corresponding biochar increased with the pyrolysis temperature rise, and the O/C molar ratio was between 0.01 and 0.08. The increase in H/C molar ratio and the decrease in O/C molar ratio indicate a gradual aromatization enhancement. Straw A has a higher nitrogen content in biochar (nitrogen application rate) compared with straw B.

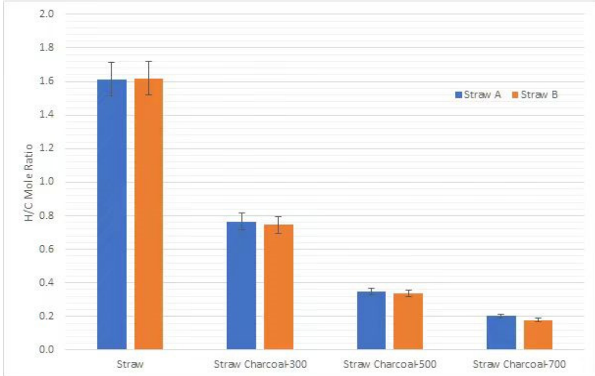

Figure 4 The H/C of biochar

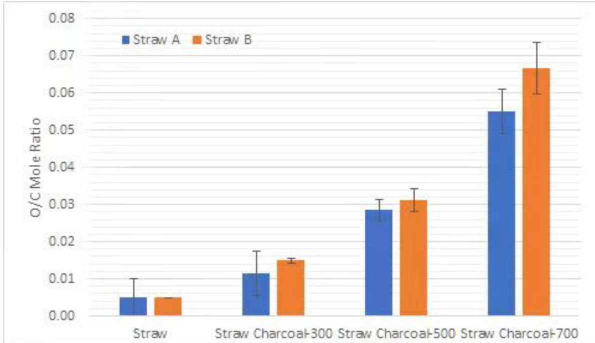

Figure 5 The O/C of biochar

3.4.Biochar MRT value

The MRT (Microbial Residence Time) value of biochar has trend as Figure 6. The straw B has higher value than straw A, especially in the condition of 700 ℃. The MRT values of straw A and straw B show that straw B can be kept longer in the soil. As a kind of fertilizer, biocarbon is a better property to stay in the soil for a longer time. Therefore, it can be seen that straw B is more conducive to the soil than straw A at the incineration temperature above 500 degrees Celsius. The straw biocarbon generated by the incineration temperature of 700 degrees has the strongest persistence, and the value at 700 degrees is much higher than 500 degrees, which is very different from other values, but in the consideration of pay and return, 500 degrees is a more suitable incineration temperature.

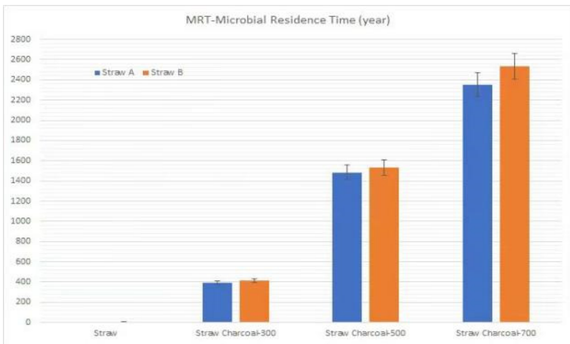

Figure 6 The MRT value of biochar

4.Discussions

One important experimental independent factor is the temperature used for pyrolysis of biochar. When the straw heat was converted into biochar, the pyrolysis temperature was 100~200 ℃. Since the organic matter failed to be pyrolyzed, the water vapor lost, so the content of total carbon and total nitrogen changed little. When the pyrolysis temperature reached 300 ℃, cellulose and hemicellulose were decomposed, especially the carboxyl and carbonyl groups in hemicellulose were decomposed, and a large amount of H_2O, CO_2 and CO were released, which correspondingly increased the total nitrogen content slightly. As the pyrolysis temperature increased, the decomposition of organic matter intensified, oxygen was consumed, and residual carbon rich substances were left, improving the relative total carbon content of rice straw charcoal. The influence of temperature on biochar, and can be took as supplements and interprets to support the analysis of the different physical and chemical effects produced by biochar at different pyrolysis temperatures.

pH value is a significant property of biochar. In this study, the pH value of rice straw after carbonization increased with the pyrolysis temperature rise, which was consistent with the research results reported by other researchers. There are two main reasons: On the one hand, as pyrolysis temperature increase, cellulose and lignin decompose rapidly, and biochar volatilizes and loses. Meanwhile, alkaline mineral elements such as potassium, calcium, magnesium, etc. are enriched in the ash in the form of oxides or carbonates, rapidly increasing pH value; On the other hand, the biochar surface is rich in considerable oxygen-containing functional groups. As pyrolysis temperature increases, the number of acidic oxygen-containing functional groups on the surface of biochar decreases significantly, while the number of alkaline oxygen-containing functional groups increases. Biochar is highly alkaline, which increases the soil pH value, and indirectly reduces the bioavailability of heavy metals. Moreover, biochar can change soil moisture and aeration, and affect soil oxidation and reduction potential, thus alleviating the toxicity of some charge sensitive toxic heavy metal. Biochar has a higher aromatization degree with pore structure. When heavy metal ions are close to the benzene ring, the electron cloud of the benzene ring polarizes and generates a weak electrostatic effect, causing physical adsorption. Biochar can also achieve chemical adsorption of heavy metals through surface functional groups. The hydrogen content of rice straw biochar is insufficient. Although the effect of hydrogen on plant growth is less obvious than do carbon, nitrogen, phosphorus and potassium, as agriculture advances, hydrogen can also help production. Hydrogen water can alleviate copper stress by increasing the pore diameter and maintaining cell integrity, thus promoting plant growth (Zhou et al, 2011).

To summarize, corn straw charcoal has a high pH value, and the biochar generated under high temperature is alkaline, which improves acidic soil, and corn straw charcoal contains numerous mineral elements (Zhou et al, 2011[22]). It can be inferred that biochar can also increase the content of mineral nutrients in soil, and improve soil fertility and quality. As the temperature increases, the carbon skeleton pore structure of biochar becomes clear and evenly distributed, the specific surface area increases, the microporous structure becomes more abundant, the oxygen containing functional groups continue to decrease, the alkaline groups increase, the aromaticity and the stable carbon ring structure increase, thus enriching the essential nutrients for crop production. The biochar in farmland has great carbon fixation potential and space. The biochar application may uniquely and technically change the natural balance of soil carbon pool in the ecosystem and improve the capacity of soil carbon pools by inputting stable carbon sources. Biochar itself is a significant form of "carbon sink," which provides a technical way to achieve carbon sequestration, emission reduction and sustainable agricultural development.

5.Conclusions

Recently, with more and more attentions on biochar research (Chen et al, 2013 [3]), there are different methods and conditions have been studied, except the focus of pyrolysis temperature impacts on different chemical effects, my research explored the factors from soil fertility and quality, and tried to identify the optimal soil fertility conditions through the property analysis of biochar and thus guide fertilization.

The biochar research is becoming more and more popular, it is important to help to reduce the carbon emission, we need figure out the effective way to change the natural balance of soil carbon pool in the ecosystem and improve the capacity of soil carbon pools by inputting stable carbon sources. Biochar itself is a significant form of "carbon sink," which provides a technical way to achieve carbon sequestration, emission reduction. My research proves that the nutritional composition and time we pay when planting crops can also affect the abandoned parts of the crop after maturity, which proves the importance of reuse of these straws, and illustrates the necessity and value of continuing research in the field of biological carbon. From the perspective of biological carbon field, reduce, use and recycle focused on the experiment, research and discussion, laying the foundation for the future environmental protection work.

In future studies, the influencing factors of biological carbon still need to be found through a lot of experiments. My research proves the influence of land fertility on the nature of straw biological carbon, so that future researchers can have one more reference. The search for the influencing factors of biocarbon is closely related to the application of biocarbon.

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