Preparation of an Environment-friendly Biochar Fertilizer

Xuan Zhong¹, Mingfeng Wang¹ and Enchen Jiang¹,*

¹College of Materials and Energy, South China Agricultural University, Guangzhou 510642, China
*Corresponding author

Abstract. Combining biochar with urea can not only enhance the release efficiency of urea, but also improve the soil environment thus promoting the growth of plant. However, the low mechanical strength and overuse of binder have limited the improvement of the biochar fertilizer (BF). An novel BF was prepared by putting the mixture of biochar and urea into a molding tube with diameter of 6-12mm and heating at 155°C. Molten urea (155°C) was used as binder to combine with biochar in a way of heterogeneous permeation & integration. The maximum compressive strenght of BF samples with different diameter are in the range of 46.34-108.54N, much larger to that of pure urea (12.1N). The leaching experiments show that only 19.5%-33.5% of BF samples released at the first day, exhibiting a slow-release property. Therefore, our study has demonstrated the potential of this novel BF for improving the effectiveness of fertilizer.

Keywords: Biochar fertilizer; Molding; Slow-release

1. Introduction
Urea is one of the most important commercially available nitrogenous fertilizers, however, its low utilization efficiency have caused a lot of environmental problems. Biochar is a kind of multifunctional material with abundant pore structure and a large specific surface area [1]. Combining biochar with urea can not only enhance the use efficiency of urea, but also improve the soil environment and promote the growth of plant, showing a great significance for our agricultural development [2]. At present, the molding way of biochar and urea mainly includes extruding granulation [3], solid-liquid adsorption [4], rolling granulation and spraying granulation [5] etc. However, due to the hydrophobic of biochar, it’s difficult to form granulation without binder, or which the effect on the soil is still unknown. Compared with biochar, the nature of fertilizer is more simple and easy to control. Solid urea can turn into molten urea when the temperature is higher than 132.7°C and get a good fluidity property. Based on this, Ni et al. [6] produced a economic slow-release fertilizer by mixing bentonite and organic polymer into the melting urea. However, to our best knowledge, the method of mixing biochar with molten urea has not been reported yet.

This study attempted to prepare a novel BF through melting the urea as binder with biochar. In order to investigate the molding process, the mechanical property and the content of biuret of different BF samples with diameter of 6mm, 8mm, 10mm and 12mm were tested. Finally the release behaviors of BF samples were evaluated.

2. Materials and Methods
Rice husk is used as feedstock for the preparation of biochar. The rice husk used is from Meizhou, China. The feedstock is grinded and then sieved through a 60 mesh before dried at 105°C for12 h. Anhydrous ethanol (AR), urea (AR), biuret (AR), copper sulfate(AR), Potassium tartrate (AR), and 4-dimethylaminobenzaldehyde ((AR)) have been used in this work.
Biochar were produced using self-designed slow pyrolysis reactor heated by commercial electric furnace (KSJD-6.3-12, ShangHai Yifeng Company, China). Approximately 100 g of rice husk was added into the quartz tube (φ30mm×L1050mm), which was accessed N2 to isolate air in the whole process. The raw materials were charred for 30-90min, and then different biochars were obtained with target temperature of 550°C after cooling to room temperature and the rest of the volatile matter were burned directly. The resulting biochar was characterized for basic chemical properties, including pH, electrical conductivity (EC), and proximate analysis following the “Standardized Product Testing Guidelines for Biochar”.

The BF samples were prepared as followed: 60% of rice husk biochar was mixed with 40% urea (w/w) for 10 minutes by glass rods. The mixed components were put into a molding tube with a diameter of 6, 8, 10, 12 mm and then preheated in temperature of 130°C for about 5min. Afterwards, rising the temperature to the molding temperature of 155°C and kept for 15 minutes. The molding process is over when molten urea and biochar are fully infiltration. Then the BF samples were squeezed out and cooling down at room temperature. And the final products with different diameter were obtained. Figure1 shows the process of preparation of BF particles.

![Diagram](image)

**Figure1.** Preparation process of BF prepared by heterogenous permeation&integration

The content of biuret was determined according to the method for the determination of biuret in the urea in the Specialised Standard of People’s Republic of China (GB/T 2441.2-2010): A 10g sample of solid urea were placed in a volumetric flask with 100mL, then the flask was transferred to a vacuum oven which the final temperatures were set at 140°C, 145°C, 150°C and 155°C respectively, and the residence time was set at 15 min. The compound of urea after heating together with solution of copper sulfate and potassium tartrate were detected using a spectrophotometer (Youke Company, Shanghai). The content of biuret was calculated according to the formulation (1):

\[
\omega = \frac{(m_1 - m_2) \times 10^{-3}}{m} \times 100 = \frac{(m_1 - m_2)}{m \times 10} \tag{1}
\]

Where \(\omega\) was the content of biuret, %; \(m\) was the mass of solid urea, mg; \(m_1\) was the mass of biuret in urea, mg; \(m_2\) was the mass of biuret in blank test, mg.
The mechanical properties of the BF samples were inferred from a stress-strain curve, obtained by a Universal testing machine (WD-100KE, Guangzhou). The BF samples were placed horizontally under the compression bar. The initial grip separation was set at 0.5mm and the test and postset speeds set at 2 and 10mm/min, respectively. Each test was performed in triplicate.

Experiments of release behavior of urea from BF samples were carried in a leaching tube at ambient temperature. Each prepared particles of BF-6, BF-8, BF-10 and BF-12 samples were placed at a depth of 80mm in the leaching tube. After 24h incubation, 100ml deionized water were poured into the leaching tube this produced leachate. Every BF samples were repeated three times and the whole leaching experiment was carried out seven days.

The absorbance level of released urea from BF samples was obtained by analyzed leachate via UV1901PC (Youke Company, Shanghai). The urea in the leachate was determined after the addition of 4-dimethylaminobenzaldehyde (4-DMAB) at a wavelength of 430nm (Chinese national standard GB/T 23348-2009 Slow release fertilizer). The calibration curve of the urea was prepared and the unknown concentration of urea in the leachate was calculated according to formula (2). The leaching process was repeated every 24h and the whole experiment was carried out seven days. Each sample was repeated three times.

\[
Abs = 0.0014C_t + 0.00009 \tag{2}
\]

Where \(C_t\) was the unknown concentration of urea, mg/L, \(Abs\) was the absorbency value and the coefficient of determination \((R^2)\) was 0.9999.

3. Results

3.1. Raw Material and Its Biochar Properties

| Sample       | C   | H   | O   | N   | S   | M   | M (%) | V (%) | A (%) | FC (%) | ce (%) | he-ce (%) | Lignin | pH | EC (ms/cm) |
|--------------|-----|-----|-----|-----|-----|-----|-------|-------|-------|--------|--------|----------|--------|-----|------------|
| Rice husk    | 42.06 | 5.69 | 51.39 | 0.82 | 0.03 | 10.54 | 66.5  | 12.3  | 10.58 | 31.3   | 24.2   | 14.3     | --     | -- | --         |
| Biochar      | --   | --   | --   | --   | --   | 3.71  | 20.0  | 30.0  | 46.16 | --     | --     | 9.95     | 0.74   |     |            |

(M-moisture, V-Volatile matter, A-ash, FC-fixed carbon, ce-Cellulose, he-ce-Hemicellulose)

The component analysis (cellulose, hemicellulose and lignin) was determined by the method of acid hydrolysis, the results show that the rice husk has more content of cellulose and hemicellulose. Proximate analysis of rice husk and its biochar show that content of moisture and volatile matter decrease after pyrolysising, while the content of ash and fixed carbon increase. The biochar dissolve in water show alkalinity with pH of 9.95 and the EC is 0.74ms/cm.

3.2. The Effect of Temperature on the Content of Biuret

The content of biuret is an important indicator to evaluate the eligibility of urea products. Figure 2 presents the content of biuret in urea at different heating temperatures. The content of biuret increase with the increase of the heating temperature in the same period. The maximum formation amount of biuret is 46mg at 155°C, which is 0.46% of the total mass of urea. According to Chinese national standard GB 2440-2001, the urea is excellent agricultural products only under the condition of the content of biuret in the urea is less than 0.9%. Therefore, the BF samples obtain in this experiment have no negative effect on the quality of urea.
Figure 2. Effects of heating temperature on the formation amount of biuret in urea

3.3. Mechanical Properties of BF Samples
Figure 3 shows the maximum compressive strength (MCS) of urea (d = 2.5mm) and four BF samples with different diameters of BF-6, BF-8, BF-10 and BF-12 BF. The MCS of all BF samples are in the range of 46.34-108.54N, which is larger than that of granular urea (12.1N). This is mainly due to the addition of biochar that has increased the stacking density of the fertilizer. In addition, the increase in the size of BF led to the MCS of BF increase first and then decrease. This is probably because larger size of BF extend the permeation time of molten urea during molding process, causing the molten urea penetrate unevenly in the biochar in the same period and temperature so that reduced the MCS of BF samples.

Figure 3. Effects of particle size on the mechanical properties of BF and granular urea

3.4. Release Behavior of BF Samples
Fig.4 presents the release behaviors of pure urea and BF samples in quartz sand at ambient temperature (25°C). At the first leaching time, about 67.32% of nutrient release from the pure urea, whereas all BF samples show an obvious reduction in the nutrient release (about 20%-40%) as the hydrophobic of the biochar surface could restrain water into the internal of BF samples. Interestingly, BF samples could further release at the 7th day compared to that pure urea (saturated at 2nd day), which indicating that BF samples show a excellently slow-release property.
4. Conclusion
In summary, a new type of environment-friendly BF was prepared and tested. The result of this work can provide a new method to reduce the use of binder and enhance the mechanical strength of BF. The data presented in this study show that the mechanical property of the BF samples is excellent compared to that of granular urea. The content of biuret is less than 0.46% of 10g sample at 155°C, smaller than that of standard of excellent agricultural urea. Finally, leaching experiment show that BF samples with different diameter exhibit an excellent slow-release property, especially for BF with diameter of 10mm.

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6. References
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