Investigation of Preparation of Biochar-based Sustained release Fertilizer from Filter Mud of Sugar Mills and Its Properties

Min Xiang1, Faqiu Liu2, Shaoji Zhou1,*, Qiuping Tang1 and Kai Li1
1School of Light Industry and Food Engineering, Guangxi University, Nanning 530004, China
2Guangxi Rural Investment Group One Another Seven Agricultural Supply Chain Co, Ltd., Nanning 530000, China

*Corresponding author

Abstract. In order to make better use of the filter mud from sugar mills, biochar was prepared by pyrolysis of the mud at 500 °C, which was then to absorb urea to produce sustained release fertilizer pellet, using soluble starch as the binder. The pellet shaping, the mechanical properties and the sustained-release effect of the pellet fertilizer were studied. The results showed that 22-26% water content was favorable for pelleting the biochar-based fertilizer, improving the maximum crushing compression force (MCCF) of the pellet. The pelleting rate and its MCCF decreased with the increase of biochar content. The sustained release effect of the pellet fertilizer was better than that of traditional fertilizer, and the sustained release effect increased with the increase of biochar content and soluble starch content. The optimum conditions in terms of pelleting rate, MCCF, sustained release performance and cost-effectiveness were the ratio of urea to biochar of 1:5, the content of soluble starch 10% and the amount of water 24%. The release of the biochar-based fertilizer was in accordance with the first-order release model.

Keywords: Filter mud; Sustained release; Biochar; Biochar-based fertilizer.

1. Introduction
The use of natural fertilizers has increased the output of agricultural products, but there are still many problems such as excessive fertilization of land, or the utilization rate of fertilizers are relatively low and so on [1]. Since there are about 700 million tons of biomass waste in China every year that causes waste of biomass resources and environmental pollution [3-5].

Biochar is a kind of carbon which can be obtained by pyrolysis of biomass materials such as rice straw and sawdust under the condition of limiting or isolating oxygen. It is called biochar because of the fixed carbon in it [6-7]. Because of its high ash content, biomass carbon made from rice straw and other wastes are limited in other industrial application fields, but its application in agriculture can complement each other and maximize its value [8-9]. In recent years, much study has been done on the preparation of sustained release fertilizer from biomass materials. For example, Zhu et al. [10] prepared a double-coated urea fertilizer with both water-absorbing and water-retaining function and sustained release function. Zhang [11] used rice straw char as the matrix to prepare two different types of biochar-based sustained release fertilizer, granular and columnar pellets, which showed significant improvement compared with traditional fertilizer. Jiang [12] also used rice straw char as the matrix and kaolin as binder to prepare granular sustained release fertilizer, the results showed that the cumulative
release rate of the fertilizer reached 5 times. Cui et al. [14] studied the effects of adding granular activated carbon and two kinds of sustained release biochar-based fertilizers for the growth of maize. The results showed that the yield of using the sustained release biochar-based fertilizers increased by 13% on average compared with ordinary fertilizers. Li et al. [15] studied the effects of two kinds of sustained release fertilizers on the yield of tomato in greenhouse. Khan et al. [16] developed a kind of charcoal sustained release fertilizer, observed its morphology by SEM and simulated the release mode of fertilizer. However, there are few reports on the preparation of biochar-based sustained release fertilizer using filter muds from cane sugar production as the char matrix.

Filter mud is one of the three major by-products of sugar mills, accounting for 3-4% of the cane processed. It is a large volume waste to be disposed by the sugar mills. As a conventional treatment, most of the mud is made back to the field as a harmless disposal. But recently it is becoming more and more unwelcomed by farmers in China. The primary reason for this is that it is hardly effective as an agricultural fertilizer. It generates intense heat (65 °C), foul odor and takes long time for natural decomposition, furthermore, it is inconvenient for transportation and application, having water content around 70-80%.

In this paper, biochar was prepared by pyrolysis the filter mud, soluble starch was used as binder, urea was used as fertilizer, the shaping effect, maximum compressive strength and leaching effect of fertilizer were measured, the shaping situation, mechanical properties and sustained release effect of fertilizer were studied, which provided reasonable technical support for the preparation and production of filter peat-based sustained release fertilizer.

2. Materials and Methods

2.1. Materials
Filter mud was obtained from LIANGCI SUGAR Manufacturing Co. Ltd (Guangxi, China), which is preserved in refrigerator after being dried to avoid deterioration over time.
Urea, Soluble starch, Anhydrous Ethanol, P-dimethylamino-benzaldehyde, Sulfuric acid, 1-2 mm diameter Quartz Sand and other chemicals purchased from local suppliers were of analytical grade.

2.2. Methods

2.2.1. Preparation of Biochar. Filter mud were dried to a constant weight, and then a certain amount of it was weighted and put into crucibles, which were wrapped by two layers of aluminum foil and tinfoil paper to isolate oxygen and put into the muffle furnace. The biochar was prepared by carbonization at 500 °C for 4h by oxygen-limiting pyrolysis and then was taken out to a dryer after the muffle furnace was cool to room temperature. The samples were crushed and screened through a 80 mesh (0.2 mm) sieve and stored in sealed bags.

2.2.2. Preparation of Biochar-based Fertilizer. A certain amount of urea (1:1, 1:2, 1:3, 1:4, 1:5 with the mass of biochar) and soluble starch (5%, 10%, 15% of the total mass) were weighted and dissolved in distilled water (20%, 22%, 24%, 26%, 28% of the total, respectively), and then the biochar was added and mixed according to different biochar-urea ratio. The samples were put into the pellet mode (Zhangzhoutongfu, SKJ-120) for extrusion for pelleting. The obtained pellets were dried at 40 °C to constant weight (Figure 1).
Figure 1. The pelleting rate and the formed biochar-based urea sustained release pellet fertilizer.

2.2.3. Test of Pelleting Rate and Maximum Crushing Compression Force (MCCF). The complete formed biochar-based fertilizer particles with diameters about 1-6mm were selected out, and the pelleting rate was determined by equation (1),

\[
\text{pelleting rate} = \frac{w_1}{w_2} \times 100
\]

where, \(w_1\) is the mass of complete biochar-based fertilizer pellet with diameters about 100mm, \(w_2\) is the total mass of all materials.

The MCCF measurement of the samples were carried out on the TMS-PRO texture analyzer (FTCCo., Ltd, USA). The probe of the texture analyzer was selected with a measuring range of 100 N, the probe's descending speed was set at 120 mm/min, and the minimum testing force was set at 0.05 N. The MCCF on the biochar-based fertilizer was recorded, and each sample was measured for three times and a arithmetic mean was obtained.

2.2.4. Leaching Experiment. The sustained release effect of biochar-based fertilizers was tested according to the testing standard GB/T23348-2009. PVC pipes with inner diameter of 3cm and height of 30 cm were used, the bottom of which were sealed by double-layers wrapping with 100 Mesh Gauze. In each pipe, 30g of quartz sand was placed at the bottom, 1g of biochar-based fertilizer was then added, on top of which another 20g of quartz sand was covered. The experimental rig is shown in Figure 2. The experiment was carried out by adding 50 mL of distilled water constantly within 2 minutes to each pipe at every 24h interval to simulate rain fall, then the leaching solution was collected in 250 mL conical flasks, the content of urea in the leaching solution was determined by P-dimethylamino-benzaldehyde color Spectrophotometer. The volume of the leaching solution, \(V\), was measured, and the concentration of urea in the leaching solution, \(C\), was determined by a UV spectrophotometer (Zhonghuitiancheng ZH1771). All experiments were replicated at least 3 times. The quantity of urea in the leachate, \(M\), was calculated according to equation (2).

\[
M = V \times C
\]

The quantity of urea in the leachate divided by the total urea quantity in the fertilizer is the single releasing rate, and the cumulative single releasing rate is the cumulative releasing rate.
3. Results and Discussing

3.1. Factors Affecting the Pelleting of the Biochar-based Fertilizers

3.1.1. Effect of Dosage of Biochar and Water. The addition of water and biochar plays an important role in the formability of biochar-based fertilizer. The content of soluble starch was set as 10%, and the addition of water was 20%, 22%, 24%, 26% and 28% respectively and the mass ratio of urea to biochar was 1:1, 1:2, 1:3, 1:4 and 1:5 respectively. Then the process of pelleting and drying was carried out and the pelleting rate and the MCCF was determined. The results are shown in Figure 3 and 4 below.

![Figure 3. Effect of water addition and mass ratios of urea to biochar on pelleting rate.](image)

![Figure 4. Effect of water addition and mass ratios of urea to biochar on MCCF.](image)

As shown in Figure 3, for given mass ratio of urea to biochar, the pelleting rate was first increased and...
then decreased with the increase of water addition, this may be due to the viscous effect caused by the mixing of soluble starch with water in the pelleting process, which was favorable to pelleting. But when the addition of water was excessive, the biochar-based urea became overgraining, resulting in the pelleting becoming difficult[11]. For given water addition, the pelleting rate decreased gradually with the increase of the proportion of biochar. This may be due to the char having large porosities and specific surface areas, and with the increase of the amount of char, there were more porosities and surface area and much water was demanded[12]. In this experiment, when the ratio of urea to biochar was 1:1 and the amount of water addition was 22%, the pelleting rate of biochar-based fertilizer reached the maximum of 74.5%.

As can be seen from Figure 4 that with the increase of water addition, the MCCF of fertilizers with different ratio of urea to biochar first increased slightly and then decreased slightly, reaching the maximum value when the water addition was 24%. When the ratio of urea to biochar was 1:1, the crushing force reaches the maximum value of 20.45 N, and when the ratio of urea to biochar is 1:5, the maximum crushing force is reduced to 7.59 N. The larger the proportion of biochar, the more significant the deduction of the MCCF of the pellet fertilizer. Under each water addition condition, when the ratio of urea and biochar was 1:1, the MCCF of the fertilizer was the highest, which showed that the pelleting effect and compressive strength of the fertilizer were the highest in this case.

3.1.2. Effect of Soluble Starch Addition. When the addition ratio of urea to biochar was 1:1 and the addition of water 24%, the variations of pelleting rate and the MCCF with the soluble starch content is shown in Figure 5.

![Figure 5. Effect of soluble starch addition on pelleting rate and MCCF.](image)

As shown in Figure 5, The pelleting rate and the MCCF of the pellet fertilizer increased significantly at the beginning and then become gradual increase with the increasing of soluble starch content, the turning point was at 10%. As the increase of soluble starch content will lead to the reduction of effectiveness of biochar-based pellet fertilizer while wasting the soluble starch, it was reasonable to choose the content of soluble starch as 10%.

3.2. Analysis of Release Properties of the Biochar-based Fertilizer

3.2.1. Effect of Biochar on Sustained Release. When the addition of soluble starch and water were set as 10% and 24% respectively, the variation of single release rate and cumulative release rate with the ratio of urea to biochar is shown in Figure 6. As is shown in Figure 6 that the release rates of biochar-based urea was significantly lower than those of pure urea. After the first leaching, the pure urea release rate was 75%, while that of the biochar-based urea with urea to biochar ratio of 1:1 was 38.64%, with urea to biochar ratio of 1:5 being 18.43%, with the reduction of 36.36% and 56.57% respectively. Compared with pure urea after the second leaching with the cumulative release rate of fertilizer basically reaching100%, other fertilizers with different proportions of biochar basically...
dissolved all the urea after the sixth leaching, indicating that the addition of biochar can improve the sustained release property of fertilizers. With the increase of the amount of biochar, the cumulative release rate of urea gradually decreased, indicating that with the increase of the proportion of char. The sustained release effect increased correspondingly. This is due to adsorption of dissolved urea by the carbon during the mixing process which made the urea molecules migrated to the mesopores and micropores of the biochar that formed a capillary, which played a sustained release role.

![Figure 6. Effect of different ratio of urea to biochar on cumulative.](image1)

![Figure 7. Effect of different soluble starch addition on cumulative release ratio of urea.](image2)

3.2.2. Effect of Soluble Starch on Sustained Release. The results of leaching experiments of the pellet fertilizer with 5%, 10% and 15% soluble starch addition were shown in Figure 7. The first release rate of the pellet fertilizer with the soluble starch content of 5% was 30.46%, and those of the pellet with the soluble starch contents of 10% and 15% were 18.43% and 17.47% respectively. This showed that with the increase of starch soluble content, the viscosity became greater after dissolving in water, and the pellets became more compact, resulting in greater resistance for the urea to migrate to the surface, thus the leaching time became longer. All the three biochar-based fertilizers with different starch soluble content basically released all the urea after the sixth leaching. From Figure 7 it could be also seen that there was no significant difference in the cumulative release of urea the soluble starch content was 10% and 15%, therefore it was reasonable to choose the starch soluble content of 10%.

3.3. The Release Model of the Biochar-based Fertilizer
The release kinetics equation was used to fit the release figures of the filter mud biochar based pellet fertilizer. The common release models were zero-order release model and first-order release model. So the zero-order release model and first-order release model were selected to fit the release curves of the biochar-based pellet fertilizer under different conditions.
3.3.1. Zero-order Release Fitting. The zero order release model of \( y = a + bx \) is used to fit the sustained release under different conditions. The fitting is carried out using the Origin 8.5, the results are shown in Table 1. The correlation coefficients of the fitting are less than 0.93, indicating that the release figures are not in accordance with the zero-order release model, which means that the release does not belong to the constant rate release.

| Condition                          | Samples       | fitting equation         | \( R^2 \) |
|------------------------------------|---------------|--------------------------|-----------|
| Different ratios of urea to biochar| 1:1           | \( y=28.6308+12.7612x \) | 0.7236    |
|                                    | 1:2           | \( y=21.3350+12.8175x \) | 0.8197    |
|                                    | 1:3           | \( y=17.7708+14.1766x \) | 0.8627    |
|                                    | 1:4           | \( y=13.9533+14.6619x \) | 0.8913    |
|                                    | 1:5           | \( y=11.2492+14.9838x \) | 0.9102    |
| Different additions of soluble starch | 5%           | \( y=21.4108+13.6512x \) | 0.8241    |
|                                    | 10%           | \( y=11.2491+14.9838x \) | 0.9102    |
|                                    | 15%           | \( y=9.8492+14.9685x \)  | 0.9273    |

3.3.2. First-order Release Fitting. The first-order release model is \( \ln(1-M_t/M_\infty)=-kt \), the equation can be converted to \( M_t=M_\infty(1-e^{-kt}) \). In this equation, \( M_t \) is the cumulative release at time \( t \) and \( M_\infty \) is the cumulative release at time \( \infty \). Table 2 shows the fitting results.

| Condition                          | Samples       | fitting equation         | \( R^2 \) |
|------------------------------------|---------------|--------------------------|-----------|
| Different ratios of urea to biochar| 1:1           | \( y=102.5337(1-e^{-0.5744t}) \) | 0.9899    |
|                                    | 1:2           | \( y=109.3607(1-e^{-0.4064t}) \) | 0.9929    |
|                                    | 1:3           | \( y=113.9955(1-e^{-0.3389t}) \) | 0.9933    |
|                                    | 1:4           | \( y=122.2089(1-e^{-0.2754t}) \) | 0.9879    |
|                                    | 1:5           | \( y=131.2894(1-e^{-0.2311t}) \) | 0.9835    |
| Different additions of soluble starch | 5%           | \( y=108.0417(1-e^{-0.4103t}) \) | 0.9922    |
|                                    | 10%           | \( y=131.2894(1-e^{-0.2310t}) \) | 0.9858    |
|                                    | 15%           | \( y=137.2518(1-e^{-0.2056t}) \) | 0.9880    |

The correlation coefficients \( R^2 \) of the first-order release model are more than 0.98, thus the release of biochar-based fertilizer are in accords with the first-order release model, which also means the release mechanism is internal diffusion.

4. Conclusions
The biochar based fertilizer from filter mud of sugar mills that has been investigated by the authors and the conclusions are listed as follows:
The amount of water of 22%-26% is favorable to the pelleting of the filter mud biochar-based fertilizer in terms of improving the MCCF. The more biochar content, the lower the pelleting rate and the MCCF of biochar based fertilizer.

(2) The sustainable release effect has been observed by the authors in the paper, which is obviously better than that of traditional fertilizer and is better with the increase of biochar content and starch soluble content.

(3) The optimum condition for preparing the filter mud biochar-based pellet fertilizer is that the ratio of urea to biochar is 1:5, the content of starch soluble 10% and the amount of water 24%.

(4) The release of biochar-based fertilizer belongs to the first-order release model, and thus its release mechanism is internal diffusion. The biochar fertilizer was prepared by the authors due to first order kinetics internal diffusion. The release model show sustainable release of fertilizers.

Acknowledgement
The research is supported by National Natural Science Foundation of China with the approval number of 31760469, Guangxi Innovation Driven Development Special Foundation Project with the contract number of GuiKe AA17204092 and the Collaborative Innovation Center jointly established by the Ministry of Sugar Industry.

References:
[1] Zhang YM. Fertilizer utilization and nutrient efficient use [J]. Jiangxi Agriculture, 2017 (23): 33-33.
[2] Zhai Junhai, Gao Yajun, Zhou Jianbin. Review of controlled release/sustained release fertilizers [J]. Agricultural Research in Arid Areas, 2002, 20 (1): 45-48.
[3] Zhang Qisheng, Zhou Jianbin, Qu Yongbiao. efficient, pollution-free and resourceful utilization of agricultural and Forestry Biomass [J]. Forestry Industry, 2009,36 (1): 3-8.
[4] Bi Y Y, Gao C Y, Wang Y J, et al. Estimation of straw quantity in China [J]. Chinese Journal of Agricultural Engineering, 2009,25 (12): 211-217.
[5] Gao Liwei, Ma Lin, Zhang Weifeng, et al. quantity estimation and utilization of crop Straw nutrient resources in China [J]. Chinese Journal of Agricultural Engineering, 2009,25 (7): 173-179.
[6] Marchal G, Smith K E, Rein A, et al. Impact of activated carbon, biochar and compost on the desorption and mineralization of phenanthrene in soil[J]. Environmental Pollution, 2013, 181(6):200-210.
[7] Li Li, Liu Ya, Lu Yuchao, et al. environmental effects of biochar and its application[J]. environmental chemistry, 2011,30 (8): 1411-1421.
[8] Chen Wenfu, Zhang Weiming, Meng jun. research progress and prospect of agricultural biochar [J]. Chinese Journal of Agricultural Sciences, 2013,46 (16): 3324-3333.
[9] HAN Bin. Preparation and Application of Activated Carbon from Straw [D]. Donghua University, 2009.
[10] Zhang Baolin, Cheng Liang, et Al. preparation of sustained release fertilizers with water retention function [J]. Chinese soil and fertilizer, 2013 (3).
[11] Zhang Wei. Preparation and properties of rice straw carbon based sustained releasefertilizer [D]. Northeast Agricultural University, 2014.
[12] JIANG En-chen. Preparation and properties of granular biomass carbon-based urea fertilizer [J]. Journal of Northeast Agricultural University, 2014 (11): 89-94.
[13] Ma Huanhuan, Zhou Jianbin, Wang Liujian, et Al. optimization of extrusion granulation process and main properties of carbon based fertilizer for Straw [J]. Chinese Journal of Agricultural Engineering, 2014, 30 (5): 270-276.
[14] Yue-Feng C, Ya-Qing Z, Wen-Fu C. Applying Effect of Pellet Active Carbon and Sustained releaseFertilizer on Maize [J]. Liaoning Agricultural Sciences, 2008.
[15] Li Y, Sun Y, Liao S, et al. Effects of two sustained releasenitrogen fertilizers and irrigation on yield, quality, and water-fertilizer productivity of greenhouse tomato[J]. Agricultural Water Management, 2017, 186:139-146.
[16] Khan M A, Kim K W, Mingzhi W, et al. Nutrient-impregnated charcoal: an environmentally friendly sustained release fertilizer[J]. Environmentalist, 2008, 28(3):231-235.