Preparation and Performance Evaluation of Biochars from Neem Seed Active Substance Extracted Residues (NSASER)

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Abstract. Neem seed active substance extracted residues (NSASER) is industrial by-product, which is often discarded as a waste. It would lead to a certain degree of harm to the environment. The aim of this study was to prepare the biochars with neem seed active substance extracted residues (NSASER) under the anaerobic pyrolysis conditions. The pyrolysis process was studied with different pyrolysis power (200W, 500W, 800W, 1100W and 1400W), and the performance of the prepared biochars was evaluated. The results showed that the required time was to complete the pyrolysis process that gradually decreased with pyrolysis power increased from 200 to 1400 W, and the final pyrolysis temperature was to complete the pyrolysis process that increased with pyrolysis power increased from 200 to 1400 W. The biochars yield decreased with pyrolysis power increased from 200 to 1400 W, and the biochars yield has the maximum value when the pyrolysis power was of 200W. And the prepared biochars still had some characteristics of the plant cell and kept uniform porous structure, which was beneficial to absorb the small molecule substance. The water content of the prepared biochars was 7.18±0.53, the ash content of the prepared biochars was 5.92±0.31 and the fixed carbon content of the prepared biochars was 81.27±0.89. Compared with the bamboo charcoal, the performance index of the prepared biochars was in according with National Standard of the People’s Republic of China GBT26913-2011 of the bamboo charcoal. The prepared biochars had a potential value in application.

1. Introduction
Neem (Azadirachta indica) is a native tree, belonging to Meliaceae family which is widely cultivated in tropical and subtropical regions, including Indonesia, Burma and India. Neem has long been used as an herbal medicine in traditional country such as India and Indonesia [1]. It has long been used in traditional country so as to prevent and treat various diseases such as malaria and so on. In recent years, many modern scientific and medical studies have demonstrated that it possessed a wide spectrum of biological activities such as antibacterial and antifungal [2]. Validation studies conducted confirm that neem has been rich in much secondary metabolites such as terpenoids. Various parts of neem could be used as an herbal medicine, including leaves, root bark, stem bark and seed [3]. Among them, neem seed is most widely used as pesticides and medicine [4]. It has been proved that azadirachtin and neem seed oil were the main active substance of the neem seed, which could prevent and treat various diseases[5]. Azadirachtin is one of the best natural plant sources for the development of biological pesticides [6]. Also, Azadirachtin is widely used in medicine such as malaria, fever and fertility. Neem seed oils have a good antifertility effect, and have not yet found its toxic and side effects. It is a kind of natural plant medicine with great research and development value [7]. Usually,
the extraction of azadirachtin was carried out using solvent extraction method. In the extraction of azadirachtin, neem seed oil was also often isolated [8]. However, these neem seed active substance extracted residues (NSASER) with small amount of organic reagents are often treated simply and then thrown away. It leads to a certain degree of harm to the environment.

Biochars is a kind of carbonaceous materials by incomplete combustion of biomass materials under anaerobic or oxygen-limited conditions [9]. Biochars has the features of high carbon content, high stability, abundant surface functional groups, multiple porosity, high specific surface area and cation exchange capacity and so on, which could be used as the adsorbents for heavy metals and organic pollutants in soil and water. Also, it has the potential to fix heavy metals and organic pollutants in the soil [10], [11]. Therefore, biochars could be widely applied to many aspects such as fixing carbon, reducing discharge, retarding greenhouse gas emission, charring field, improving soil, promoting crop growth and remediation of environmental pollution [12], [13]. Biochars could be produced from much biological resources, including forest residues, agricultural waste, urban waste, yard waste and so on [14]. Neem seed active substance extracted residues (NSASER) was belonging to agricultural waste, and so it could be regarded as a raw material to be used to prepare biochars.

The aim of this study was to prepare the biochars with neem seed active substance extracted residues (NSASER) under the anaerobic pyrolysis conditions. The pyrolysis process was studied with different pyrolysis power. Then, the performance of the prepared biochars was evaluated. It makes neem seed active substance extracted residues (NSASER) be effectively utilized.

2. Materials and methods

2.1. Material

The neem seed active substance extracted residues were collected after the azadirachtin and neem seed oils were extracted.

2.2. Preparation of biochars

Preparation of biochars was usually used by direct carburation [15], and it was described by the following processes, as shown in Fig. 1. Firstly, the neem seed active substance extracted residues (NSASER) was dried by hot-air drying at 40°C. Then, the neem seed active substance extracted residues (NSASER) was smashed and then sieved through 10-mesh before use. 200 g of the neem seed active substance extracted residues (NSASER) powder was weighed precisely, and put into the self-made anaerobic pyrolysis device, as shown in Fig. 2. Subsequently, the anaerobic pyrolysis experiments were performed with a certain pyrolysis power. After that the biochars were obtained.

![Flowchart of anaerobic pyrolysis](image)

Figure 1. Flowchart of anaerobic pyrolysis

2.3. Analysis of anaerobic pyrolysis process
Effect of different pyrolysis power (200W, 500W, 800W, 1100W and 1400W) on the process was studied. The value of the change in time and temperature was record with the self-made anaerobic pyrolysis device. Also, Effect of different pyrolysis power (200W, 500W, 800W, 1100W and 1400W) on the biochars yield was studied. Weighing method was applied here to measure the biochars yield. The biochars yield (%) was calculated as following Eq. (1):

\[ A = \frac{A_1}{A_0} \times 100\% \] (1)

Where A is the biochars yield, \(A_1\) is the obtained biochars weight, and \(A_0\) is the raw material weigh.

2.4. Scanning electron microscope

The prepared biochars were coated with gold and examined with a scanning electron microscope system under high vacuum condition at an accelerating voltage of 15.0 kV, as well as image magnifications 2000 ×.

2.5. Determination of performance index of biochars

2.5.1. Determination of water content

Determination of water content was described as National Standard of the People’s Republic of China GBT26913-2011 [16]. The prepared biochars was smashed and then sieved through 18-mesh before use. 10 mL of weighing bottle was put into the drying oven, and dried at 105°C to constant weight. Then, 10 mL of weighing bottle was weighed after cooling 30 min. 1 g of prepared biochars was weighed, and placed in the above mentioned treated 10 mL of weighing bottle, which makes the prepared biochars distribute homogeneously. Then, it was put into the drying oven, and dried at 105°C for 4 h. After that it was taken out and put into the dryer for 30 min. After cooling, 10 mL of weighing bottle with the prepared biochars was weighed. The water content (%) was calculated as following Eq. (2):

\[ B = \frac{B_0 - B_1}{B_0 - B_2} \times 100\% \] (2)
Where \( B \) is the water content of the biochars, \( B_0 \) is 10 mL of weighing bottle with the biochars weight before drying, \( B_1 \) is 10 mL of weighing bottle with the prepared biochars weight after drying, and \( B_2 \) is 10 mL of weighing bottle weight.

2.5.2. Determination of ash content

Determination of ash content was described as National Standard of the People’s Republic of China GBT26913-2011 [16]. The prepared biochars was smashed and then sieved through 55-mesh before use. 30 mL of porcelain crucible was put into the high temperature electric furnace, and calcined at 800°C to constant weight. Then, 30 mL of porcelain crucible was weighed after cooling 30 min. 1 g of dried prepared biochars was weighed, and placed in the above mentioned treated 30 mL of porcelain crucible. Then, it was put into the high temperature electric furnace below 300°C, then slowly heated to 500°C for 30 min. After that it was slowly heated to 800°C for 4h. After cooling, 30 mL of porcelain crucible with the prepared biochars was weighed. The ash content (%) was calculated as following Eq. (3):

\[
C = \frac{C_2 - C_1}{C_0} \times 100\%
\]  

(3)

Where \( C \) is the ash content of the biochars, \( C_0 \) is the biochars weight, \( C_1 \) is 30 mL of porcelain crucible weight, and \( C_2 \) is 30 mL of porcelain crucible with the ash weight.

2.5.3. Determination of volatile content

Determination of volatile content was described as National Standard of the People’s Republic of China GBT26913-2011 [16]. The prepared biochars was smashed and then sieved through 55-mesh before use. 1 g of dried prepared biochars was weighed, and placed in the above mentioned treated 30 mL of porcelain crucible, which makes the prepared biochars distribute homogeneously. Then, it was quickly put into the high temperature electric furnace with 850°C, and heated for 7 min. 30 mL of porcelain crucible should be positioned above or below the galvanic measuring point. After that it was taken out and cooled for 5 min in the air. Then, it was put into the dryer to be cooled to room temperature, and then weighed. The volatile content (%) was calculated as following Eq. (4):

\[
D = \frac{D_1 - D_2}{D_1} \times 100\%
\]  

(4)

Where \( D \) is the volatile content of the biochars, \( D_1 \) is the biochars weight, and \( D_2 \) is the biochars weight after heating.

2.5.4. Determination of fixed carbon content

Determination of fixed carbon content was described as National Standard of the People’s Republic of China GBT26913-2011 [16]. The fixed carbon content (%) was calculated as following Eq. (5):

\[
E = 100 - (C+D)
\]  

(5)

Where \( E \) is the fixed carbon content of the biochars, \( C \) is the ash content of the biochars, and \( D \) is the volatile content of the biochars.

2.6. Statistical analysis
The obtained data were presented as mean ± standard deviation (SD), and all of the measurements were made in triplicate. All obtained data were analyzed using the OriginPro version 8.0 software.

3. Results and discussion

3.1. Effect of pyrolysis power on the process

For investigating the effect of pyrolysis power on the process, it was to set pyrolysis power at 200W, 500W, 800W, 1100W and 1400W, respectively. During the anaerobic pyrolysis process, the value of the change in time and temperature was recorded with the self-made anaerobic pyrolysis device. Then, the pyrolysis curves were plotted, as shown in Fig. 3. As seen from Fig. 3, the required time was to complete the pyrolysis process that gradually decreased with pyrolysis power increased from 200 to 1400 W, and the final pyrolysis temperature was to complete the pyrolysis process that increased with pyrolysis power increased from 200 to 1400 W. Under different pyrolysis power conditions, there was always a period of temperatures rising slowly at the beginning of the anaerobic pyrolysis process. That is because the moisture in the neem seed active substance extracted residues (NSASER) has absorbed heat in the evaporation process.

![Figure 3. Pyrolysis curve of different pyrolysis power](image)

3.2. Effect of pyrolysis power on biochars yield

For investigating the effect of pyrolysis power on biochars yield, it was to set pyrolysis power at 200W, 500W, 800W, 1100W and 1400W, respectively. The effect of pyrolysis power on biochars yield was as shown in Fig. 4. The biochars yield decreased with pyrolysis power increased from 200 to 1400 W. That is because there are three kinds of products during the anaerobic pyrolysis process, including the biochars, the biogas and the distillate (biomass tar and biomass vinegar). The biogas and the distillate (biomass tar and biomass vinegar) increased with pyrolysis power increased from 200 to 1400 W, which makes the proportion of biochars in all products reduced. The biochars yield has the maximum value when the pyrolysis power was of 200W.

![Figure 4. Effect of different pyrolysis power on biochars yield](image)
3.3. Scanning electron microscope of the prepared biochars
The biochars was prepared by pyrolysis power of 200W. Then, the prepared biochars were coated with gold and examined with a scanning electron microscope system. The scanning electron microscope images provide a visual evidence of the structure of the biochars. As shown in Fig. 5, the prepared biochars still had some characteristics of the plant cell and kept uniform porous structure. It was beneficial to absorb the small molecule substance.

![Scanning electron microscope image](image)

**Figure 5.** Scanning electron microscope images of the prepared biochars by pyrolysis power of 200W

3.4. Performance evaluation of the prepared biochars
The water content, the ash content and the fixed carbon content were important performance index to evaluate biochars. For evaluating the performance of the prepared biochars by pyrolysis power of 200W, the water content, the ash content and the fixed carbon content were determined by the method described as National Standard of the People’s Republic of China GBT26913-2011[16]. As a result, the water content of the prepared biochars was 7.18±0.53, the ash content of the prepared biochars was 5.92±0.31 and the fixed carbon content of the prepared biochars was 81.27±0.89, as shown in Table 1. Among all the biochars, the bamboo charcoal is one of the most widely used. As seen from Table 1, compared with the bamboo charcoal, the performance index of the prepared biochars was in according with National Standard of the People’s Republic of China of the bamboo charcoal. The prepared biochars had a potential value in application.

| Performance index | Bamboo charcoal* | Prepared biochars |
|-------------------|------------------|-------------------|
| Water content (%) | ≤9.00            | ≤12.00            | 7.18±0.53          |
| Ash content (%)   | ≤4.50            | ≤6.50             | 5.92±0.31          |
| Fixed carbon content (%) | ≥85.00 | ≥75.00 | 81.27±0.89 |

*National Standard of the People’s Republic of China GBT26913-2011

4. Conclusion
Neem seed active substance extracted residues (NSASER) is industrial by-product, which is often discarded as a waste. It would lead to a certain degree of harm to the environment. The aim of this study was to prepare the biochars with neem seed active substance extracted residues (NSASER) under the anaerobic pyrolysis conditions. The pyrolysis process was studied with different pyrolysis power (200W, 500W, 800W, 1100W and 1400W), and the performance of the prepared biochars was
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6. References
[1] Benelli G, Bedini S, Cosci F, Toniolo C and Conti B 2015 Parasitology research. 114(1) 227, 36
[2] Srinivasa K, Jagadeesh K and Revankar S P 2014 Journal of Medical and Health Sciences. 3(1) 93-96
[3] Bharali R K and Bhattacharyya K G 2015 Journal of Environmental Chemical Engineering. 3(2) 662-669
[4] Opoku A, Chaves B and De Neve S 2014 Biological agriculture & horticulture. 30(3) 145-152
[5] Betiku E, Omilakin O R, Ajala S O, Okeleye A A, Taiwo A E and Solomon B O 2014 Energy. 72 266-273
[6] Abedi Z, Saber M, Gharekhani G, Mehrvar A and Kamita S G 2014 Journal of economic entomology. 107(2) 638-645
[7] Balaji G and Cheralathan M 2014 Journal of the Energy Institute. 87(3) 188-195
[8] De Paula J A M, Brito L F, Caetano K L F N, De Morais Rodrigues M C, Borges L L and Da Conceição E C 2016 Talanta. 149 77-84
[9] Azargohar R, Nanda S, Kozinski J A, Dalai A K and Sutarto R 2014 Fuel. 125 90-100
[10] Kim K H, Kim T S, Lee S M, Choi D, Yeo H, Choi I G and Choi J W 2013 Renewable Energy. 50 188-195
[11] Huang D, Wang Y, Zhang C, Zeng G, Lai C, Wan J, Qin L and Zeng Y 2016 RSC Advances. 6(77) 73186-73196
[12] Purakayastha T J, Das K C, Gaskin J, Harris K, Smith J L and Kumari S 2016 Soil and Tillage Research. 155 107-115
[13] Ahmad M, Rajapaksha A U, Lim J E, Zhang M, Bolan N, Mohan D, Vithanage M, Lee S S and Ok Y S 2014 Chemosphere. 99 19-33
[14] Shi Y, Ge Y, Chang J, Shao H and Tang Y 2013 Renewable and Sustainable Energy Reviews. 22 432-437
[15] Kim J H, Ok Y S, Choi G H and Park B J 2015 Chemosphere. 134 435-437
[16] National Standard of the People’s Republic of China GB/T 29403-2012, “Bamboo charcoal”.

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