The Development of Durian Shell Biochar as a Nutrition Enrichment Medium for Agricultural Purpose : Part 1 Chemical and Physical Characterization

การพัฒนาถ่านชีวภาพจากเปลือกทุเรียนเพื่อใช้เป็นวัสดุปรับปรุงดินและเพิ่มธาตุอาหารสำหรับเกษตรกรรม ตอนที่1 การวิเคราะห์สมบัติทางเคมีและกายภาพ

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บทคัดย่อ

การทดลองผลิตถ่านจากเปลือกทุเรียนเพื่อใช้เป็นวัสดุปรับปรุงดินและเพิ่มธาตุอาหารในดิน ทำได้โดยเผาเปลือกทุเรียนในสภาวะไร้อากาศที่ช่วงอุณหภูมิ 400-500 องศาเซลเซียส จะได้ผลผลิต ถ่านจากเปลือกทุเรียน 3-4 กิโลกรัมต่อเปลือกทุเรียนสด 100 กิโลกรัม ถ่านจากเปลือกทุเรียนถูกบดและ คัดแยกขนาดให้มีขนาดอนุภาคอยู่ในช่วง 0.3-1.7 มิลลิเมตร และมีความหนาแน่นปรากฏ 0.3 กรัม ต่อมิลลิลิตร เมื่อทำการวิเคราะห์โดยเครื่อง XRF พบว่า เถ้าของถ่านจากเปลือกทุเรียนมีองค์ประกอบ ของธาตุฟอสฟอรัสและโปแตสเซียมมากกว่าถ่านชีวภาพจากวัสดุอื่นๆ เช่น แกลบ กะลาปาล์ม และไม้ไผ่ ถ่านจากเปลือกทุเรียนที่ได้สามารถปรับค่า pH ให้อยู่ในช่วงที่เหมาะสมได้ด้วยสารละลายน้ำส้มควันไม้ ทำให้ถ่านจากเปลือกทุเรียนหลังการปรับสภาพแล้วมีค่า pH ที่เสถียรอยู่ในช่วง 6.5-7.5 เมื่อทำการวิเคราะห์ลักษณะพื้นผิวด้วย SEM และ เปรียบเทียบกับค่าไอโอดีนตามมาตรฐาน ASTM D 4607-94 พบว่า ถ่านจากเปลือกทุเรียนมีความพรุนตัวสูงกว่าถ่านชีวภาพจากวัสดุอื่นๆ (ขนาดรูพรุน 20 µm และค่าไอโอดีน 202.32 mg/g)

Abstract

The biochar from durian shell in this research was studied as the nutrition enrichment medium for a plant growing media. The durian biochar was pyrolysed in a non-oxygen condition at 400-500 °C which yielded of 3-4 kg durian shell biochar per 100 kg of fresh durian shell. The durian shell biochar was ground and separated to the size of 0.3 to 1.7 mm with the bulk density of 0.3 g/ml. The durian shell biochar had 28% volatile matters, 57% fixed carbon, and 15% ashes content. X-ray fluorescence (XRF) was used to analyze the chemical compositions of durian shell biochar's ashes. It was found that the durian shell biochar had higher phosphorus and potassium content than other biochars such as char from bamboo, palm shell and rice husk. The pH of durian shell biochar was adjusted with the wood vinegar solution. The obtained durian shell biochar from this experiment had a stable pH value in the range of 6.5 -7.0 for 20 days of storage. The surface morphology of the durian shell biochar was determined by scanning electron microscope (SEM) and surface porosity was estimated by iodine number using ASTM D 4607-94. It was found that the durian shell biochar had pore size of 20 µm and iodine number of 202.32 mg/g which showed higher porosity than the other biochars in this study.

คำสำคัญ : ถ่านชีวภาพ , เปลือกทุเรียน , วัสดุปรับปรุงดินและเพิ่มธาตุอาหาร

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1. Introduction

The discovery of Amazonian dark earth (terra preta) has led to the use of biochar as the soil conditioner to improve crops productivities. Biochar is a char from biomass that pyrolysed in a zero or low oxygen environment for which intended to improve soil functions and to reduce green house effects by carbon sequestration [1,2]. Adding biochar to soil shows many benefits such as increasing cation-exchange capacity, retaining nutrients, improving water and nutrients retention, and reducing metal contaminants [3-6]. Furthermore, the biochar is reported to show an interesting characteristic of slow-releasing major macro nutrients (N, P, and K) which are required for plant growth [7].

Durian, as known as "The King of Fruit", is one of the most famous fruit in Thailand. The statistic data from office of Agricultural Economic shows that the Durian production in Thailand yields more than 600,000 metric tons per year during 2008-2009. Therefore, the durian shell waste can be up to 300,000 metric tons per year (considering the durian shell is 50% by weight).

Biochars are made from different raw materials such as nut shells, rice husks, and bagasse from sugar cane processing depending on the crop residues on specific location. However, not all agricultural wastes are considered good raw materials for biochar making [8]. It is reported that the most suitable green waste for high-yielded biochar production should have high lignin concentration because the formation of char from lignin occurred at a mild condition due to the breaking of relatively weak bond [9]. Durian shell has a potential to be activated carbon precursor due to its high lignin content [10]. Also durian fruit has high amount of potassium which is one of the major macro nutrient the plants needed. From these characteristic of durian makes its shell shows a fascinating material for biochar production.

The main aim of this study was to compare chemical and physical characterization of biochar made from durian shells and others biomass available in Thailand such as rice husks, coconut shells, and bamboos. Also the possibility of pH stabilization of the durian biochar was investigated.

2. Experimental

2.1 Materials

The durian shells were collected from the Marketing Organization for Farmer (MOF) in Bangkok, Thailand. The shells were sun-dried to reduce moisture content for 48 hours. The sun-dried shells were pyrolysed in a traditional kiln made from 200-liter barrel. The pyrolysis condition of the durian shells was done in an absence of oxygen, 400-500 ^{o}C and lasted for 8 hours. The durian biochar was then ground using hammer milled and sieved to 0.3-1.7 mm particle size range with the bulk density of 0.3 g/ml. The other biomasses, rice husks, coconut shells, and bamboos, were prepared at the same manner as above

2.2 Chemical Characterization

The volatile matters, fixed carbon, and ashes content of the biochars produced were characterized following standard methods of ASTM D3174-, ASTM D3175- and ASTM D3172-. The chemical compositions of all biochars in this study were analyzed using X-ray fluorescence (XRF, Fisons, ARL8410)

2.3 Physical Characterization

The morphologies of all biochars in this study were observed by scanning electron microscopy (SEM, Hitachi, S2500). The qualitative surface porosity of the biochars was estimated using iodine absorption technique from ASTM D4607-94.

2.4 Durian biochar pH stabilization

The pH of durian biochar was measured in a static condition. The grounded durian biochar weighing a total of 5 g was immersed in 50 mL of distilled water for 30 minutes. Then the mixture was filtered through filter paper (Whatman, Grade No. 1). The supernatant was measured using pH-meter (Corning, pH meter 240). The alterations of durian biochar's pH was done by mixing 200 mL of wood vinegar 10-50% v/v solution to 250 g of the grounded durian biochar and left the mixture in the ambient temperature until completely dry. To determine the pH stability, all samples were kept in an airtight container and measured pH value for 20 days in the same procedure as above. In addition, all samples were analyzed in triplicate.

3. Results and Discussion

3.1 Volatile matters, fixed carbon and ashes content of biochars

The volatile matters, fixed carbon, and ashes contents of the selected biochars are given in Table 1. The volatile matters content represented the amount of tars and releasable gasses in biochar. The fixed carbon content indicated the soild fuel and carbon content left after the volatile matter was driven off. The ashes content informed the amount of mineral matter and incombustible matter in biochars [11, 12]. Therefore, the biochar from rice husk which had 50% of ashes content should have the highest amount of inorganic mineral content than biochars made from other materials. However, the chemical composition of ashes content needed to be analyzed in details using XRF.

Table 1 The chemical content analysis of different type of biochars

Content		Type of Biochars			
		Durian Shell	Bamboo	Palm Shell	Rice Husk
Volatile Matters,	%	28	26	28	18
Fixed Carbon,	%	57	64	65	32
Ashes,	%	15	10	7	50

3.2 Chemical composition of biochars

The chemical composition analysis of different types of biochars is shown in Table 2. Interestingly, the ashes from durian shell biochar had very high amount of potassium (K) and phosphorous (P) which are the major macro nutrients required for plant growth, while the others had high amount of silica (Si) especially in rice husk biochar's ashes. The data from XRF analysis also informed that the raw materials which were the structural parts or hard protective shell of the plant contained high silica content. This explained the large fraction of silica in rice husk, palm shell, and bamboo respectively. However, the case of durian shell, the silica content was very low compared to the others while the potassium and phosphorous contents were high. When considering the durian shell structure closely, the shell had two layers, the hard and spiky outer shell and the soft and spongy inner shell. This structure of durian shell might contribute to the low silica content and high potassium and phosphorous contents of the ashes. Moreover, the chemical compositions of ashes from durian shell biochar mostly comprised of the major and minor macro nutrients beneficial to plant. Therefore, the durian shell biochar demonstrated the appealing chemical characteristic that was useful to plant than the others despite it had lower ashes content than the rice husk biochar.

Table 2 The chemical compositions of biochars' ashes analyzed by XRF

Chemical Composition (%)	Type of Biochars' ashes			
	Durian Shell	Bamboo	Palm Shell	Rice Husk
K_2O	47.24	10.35	15.89	2.15
P_2O_5	14.37	10.61	2.23	0.42
MgO	15.79	11.30	3.20	0.42
CaO	8.49	6.06	15.84	1.00
SiO_2	6.25	31.72	53.62	86.90
Fe_2O_3	1.74	27.05	3.71	0.10
SO_3	3.23	1.27	2.44	0.17
Na_2O	0.24	0.23	-	0.48
Al_2O_3	1.25	0.17	2.80	0.19
MnO	0.12	0.29	-	-

3.3 SEM analysis

The surface morphologies of different types of biochars in this study are presented in Figure 1-4. It was found that the biochars from durian shell and bamboo had high porous structure with numerous hollow cells. Contradictory the biochars from palm shell and rice husk had very rough surface with no pore. The reason for these different surface morphologies of each biochars should be the difference of cellular microstructure of each material. To serve the purpose of being the fruit's shell, the durian shell needed to be breathable and moisture controlled. To be breathable and moisture controlled, the cellular microstructure of durian shell should contain numerous interconnecting pores that allowed gasses to pass through selectively while maintained the right amount of water molecule inside. In the bamboo biochar case, the porous structure found was influenced by the water-conducting and food-conducting cells of the stem. Those cells were arranged end-to-end forming a system of tubes that conveys water and nutrients [13] which explained the systematically pores ordering in bamboo biochar. However, the pore size of the durian shell biochar was much smaller than the pores of bamboo biochar dues to the selective permeable of gasses properties. While the other shells such as rice husk and palm shell were functioned to protect the seed, the breathability and moisture controlled characteristics were different from the fruit. To protect the seed, the shell needed to be tough and not allow anything harmful to get through the seed inside. Therefore, the surfaces of the rice husk and palm should have the very rough morphology to increase surface energy and no pores to repel contaminants away.

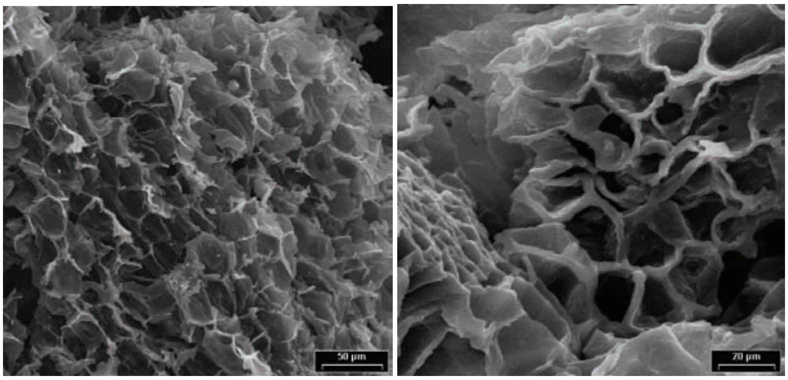

Figure 1 The SEM pictures of durian biochars' surface morphology

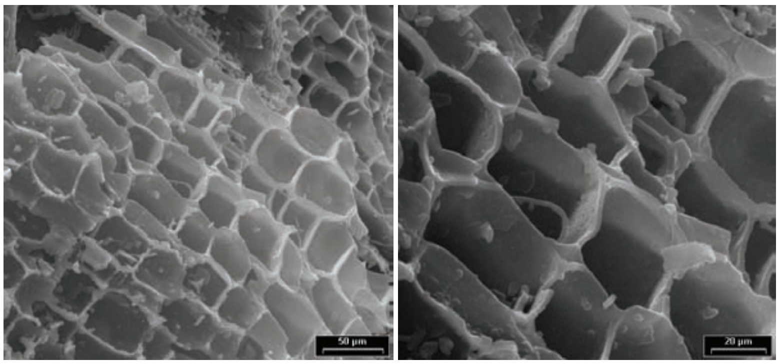

Figure 2 The SEM pictures of bamboo biochars' surface morphology

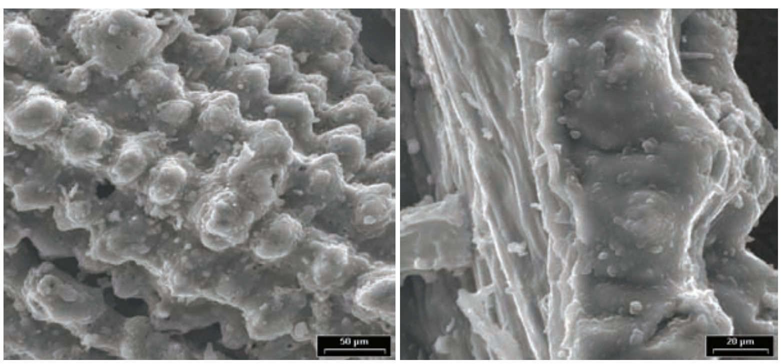

Figure 3 The SEM pictures of rice husk biochars' surface morphology

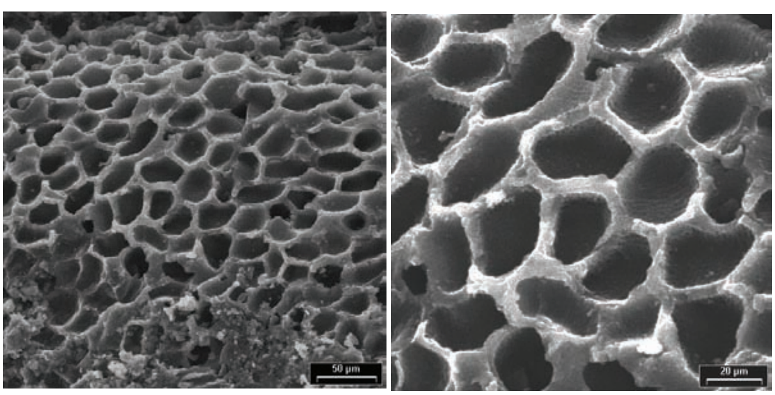

Figure 4 The SEM pictures of palm shell biochars' surface morphology

3.4 Iodine absorption analysis

The iodine absorption analysis was done to determine the surface porosity of biochars. The higher iodine number meant the higher porous on the surface which determined by iodine absorption. In the case of the activated carbon, a porous carbon uniquely famous for its high absorption activity, the iodine number was usually higher than 600 mg/g. This analysis provided a qualitative result for the level of biochars' porosity besides the quantitative results shown in the SEM pictures. The obtained iodine numbers clearly confirmed that durian shell biochar has the highest surface porosity of all other biochars in this study (Table 3). This result made the durian shell biochar a candidate for the nutrient enrichment medium used for soil because the durian shell biochar would increase the soil moisture by retaining water in it's high porous structure.

Table 3 The iodine number of different type of biochars

Type of Biochars	Iodine Number (mg/g)
Durian Shell	202.32
Bamboo	177.66
Palm Shell	162.81
Rice Husk	67.41

3.5 pH stability determination

From the data acquired on chemical and physical properties, the durian shell biochar featured the fascinating characters for being the nutrition enrichment medium in soil. The pH value of material was also an important factor to be concerned. Most plants require the pH value around 6.5-7.5. However the pH value of durian shell biochar was measured to be 10 ± 0.1. Therefore, the durian shell biochar needed to neutralize with some acid to lower the pH in the range that suitable for most plant. The wood vinegar was selected to be the acid solution for this study. The wood vinegar was a liquid by-product from vapor and smoke during pyrolysis. The pH of the wood vinegar solution used in this study is shown in Table 4.

Table 4 The pH value of wood vinegar solution

Wood Vinegar Solution Concentration (% v/v)	pH Value
50	3.17 ± 0.01
20	3.34 ± 0.01
10	3.26 ± 0.01

After mixing the wood vinegar solution with the durian shell biochar, the changes of pH value were measured in a function of storage time to determine the pH stability of the durian biochar. As shown in Figure 5, it was obvious that the pH value of the durian shell biochar treated with 50% wood vinegar solution considerable dropped to 6.5 ± 0.1 which fitted the proper range for plant growth. Also to test the pH stability of the biochar mixture, the pH of each biochar was measured after 20 days of storage. It was found that the pH of untreated durian shell biochar was dropped during day 3-5 of storage and then increased to its original pH value at 10 at the day 20. Since the pH of untreated durian shell biochar was measured to be stable at 10 ± 0.1 as discussed in the previous result, the change of untreated durian shell biochar's pH during day 3-5 of storage should come from measurement error. When consider the change of wood vinegar treated durian shell biochar, the data showed that the durian shell biochar treated with 50% wood vinegar had a slightly increase of pH when stored for 20 days while the pH of durian shell biochar treated with the lower concentrations of wood vinegar decreased. The graph showed that at the high concentration of wood vinegar the pH of durian shell biochar had drop significantly explaining the adequate amount of acid solution that can neutralized the basic durian shell biochar's surface. While at lower concentration (10% and 20%) of wood vinegar the acid concentration was not enough for the neutralized reaction to occur suddenly, but at the longer storage time the pH of the sample slowly dropped. However when considering the change of pH of all the treated durian shell biochars, it showed that the reaction was not reach its equilibrium at 20 days of storage. Therefore, the further study about the shelf life of wood vinegar treated durian shell biochar needed to be investigated for longer period of time. Though when taking the range of suitable pH for plant growth into account, it was found that the pH value of the durian shell biochar mixed with 50% wood vinegar solution was still in the range 6.5-7.0 for 20 days.

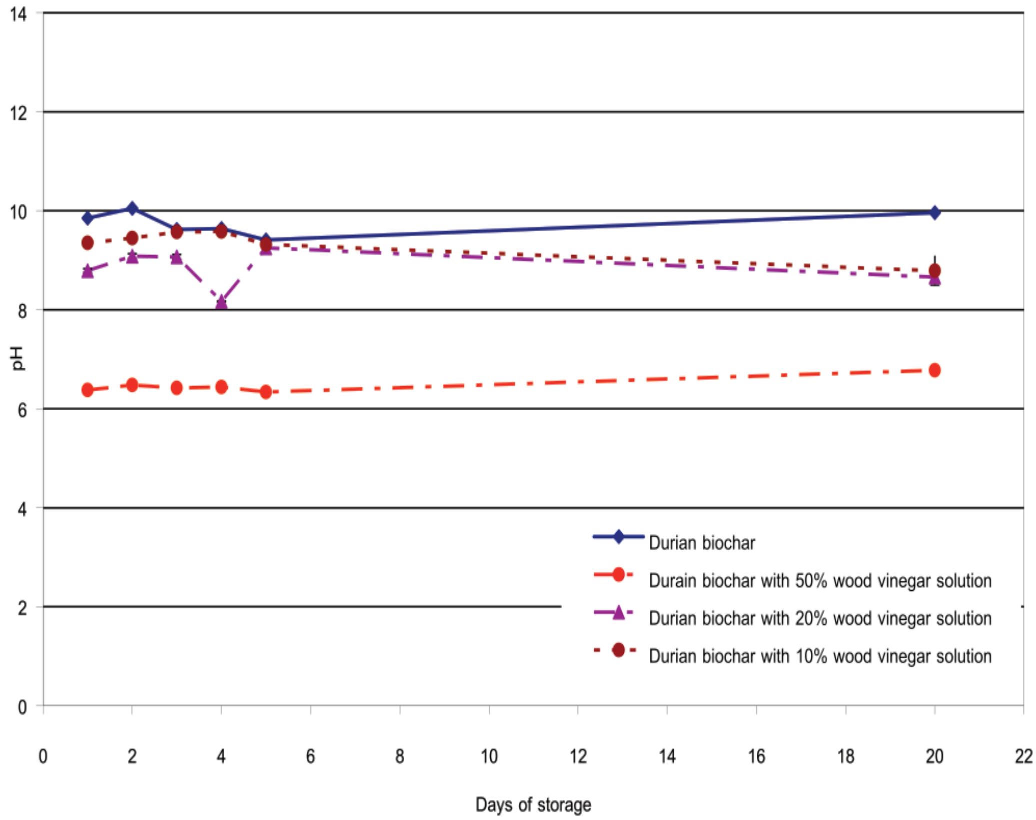

Figure 5 The stability of durian shell biochars' pH value in a function of storage time

4. Conclusion

In the present work durian shell biochar was found to have interesting characteristics which makes it the hopeful candidate for a nutrient enrichment medium in soil. The durian shell biochar has moderate inorganic contents which mostly consist of major and minor macronutrients the plant needed, especially P and K. These mineral contents in durian shell biochar make it distinguishes from other biochars made from bamboo, rice husk and palm shell. The surface properties of the durian shell biochars was investigated by SEM and iodine absorption analysis. Both techniques inform the high porosity on the surface of durian char even though the pyrolysis temperature is only at 400-500 °C. The high porous surface structure of the durian shell biochar could contribute to the high water absorption and retention which is qualify for holding moisture in soil. The high pH of the durian shell biochar can be decrease using the 50% wood vinegar solution. The pH value of the durian shell biochar after mixing with the wood vinegar solution is lower to 6.5-7.0 and stable for 20 days.

5. Acknowledgement

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