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Pyrolysis of Cassava Rhizome for Biochar Production and Characterization

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Abstract:* Pyrolysis of biomass is one of the available technologies to convert biomass into liquid, gas, and solid products. In this paper, pyrolysis method was employed to produce biochar from cassava rhizome and corn on the cob wastes. Pyrolysis experiments were carried out in a micro-cylindrical reactor, tightly sealed tubing bomb, constructed of stainless steel 316. For cassava rhizome (CR), after pyrolysis (CRA) fixed carbon surged from 18.91% to 65.35%, and ash content also rose from 6.54% (CR) to 11.25% (CRA). Nonetheless, the pyrolysis process caused sharp declines in volatile contents was 58.17% for CR as opposed to 18.7% for CRA. Based on an SEM analysis as well as an increase in iodine number from not adsorbed to 245 (CRA)), it showed that biochar produced from cassava rhizome (CRA) had highly micro porous cavity and its pore had become smaller, suitable for adsorbing minerals, microbial habitat and soil enhancement.

Keywords: **Pyrolysis, Cassava Rhizome, Biochar.**

I. BACKGROUND

Thailand boasts one of the world's largest agricultural countries with a wide range of agricultural products. As a result, there are massive amounts of agricultural wastes, almost all of which are disposed of by incineration causing substantial emission gases to the atmosphere. Recently, soil amendments from biochar (derived from agricultural wastes) have been used widely because they help augment the sequestration of carbon in soil, thereby reducing CO_2 emissions into the atmosphere [1-3]. Biochar is the carbon rich product obtained when biomass is pyrolyzed without oxygen at temperatures between 350 and 700^{O}C [4].

Many studies have been conducted on the use of biochar to improve soil conditions. Biochar is produced by biomass combustion without oxygen until it has become highly porous, then added to soil to increase its water adsorption, nutrient-holding capacity, and miCRobes. Between 2008 and 2009, there were considerable harvest areas in Thailand (especially in the northeastern region) for cassava and corn as shown in Table 1.

Table 1: Details of planting area primary crop production years 2008 and 2009. (unit: thousand tons / ha)

	2008		2009	
Type	harvest areas	yields	harvest areas	yields
Cassava	7,397	25,156	8,584	30,088

It can be seen that agricultural residues of corn and cassava were increasing from 2008 to 2009, largely disposed of by means of incineration causing dust, smoke, and pollution all over the country.

Recent studies have expanded types of agricultural wastes to produce biochar, such as bamboo, rice husk, wood chip, and wood pellets, crop residues (straw, nut shells and rice hulls) as they have different chemical properties

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and amounts of biomass residues from various agricultural areas. This paper describes the results related to the pyrolysis of biochar produced from cassava rhizome as well as the characterization of biochar formed.

II. METHODS

A. Raw materials

Cassava rhizome was collected from several places in Sakaew province, Thailand before being dried and rehydrated in an oven at 105^{O}C for 24 hours to reduce the moisture content.

1. Thermo gravimetric analysis (TGA)

The thermal behaviors of cassava rhizome and corn on the cob were studied by thermogravimetric analysis (TGA). Thermogravimetric analyses were conducted in a TGA/DSC star system (Mettler Toledo) with ramping and cooling rate of 10^{O}C/min, and nitrogen was employed as a gas carrier (100 mL/min). Approximately 20 mg. of cassava rhizome was heated under nitrogen atmosphere from room temperature to 750^{O}C.

2. The determination of physical properties

Heating values were measured in bomb calorimeter (Leco, Model AC-350) for cassava rhizome without pyrolysis (CR), cassava rhizome after pyrolysis (CRA). The values derived from proximate analysis (moisture content, percentage ash content, and percentage volatile matter content) was measured using thermogravimetric analysis (TGA) (Mettler Toledo).

3. Ultimate analysis

The amounts of carbon, hydrogen, nitrogen, oxygen, and sulfur (under ultimate analysis) were estimated by Elemental Analyzer (EA) (CHNS/O Analyzer), Perkin Elmer, model PE 2400 series II).

B. Characteristic of biochar obtained after pyrolysis

30 grams of cassava rhizome was carried out in a micro-cylindrical reactor, tightly sealed tubing bomb, constructed of stainless steel 316. The micro-reactor had the capacity of 70 ml. with inside diameter of 30 mm. The stainless steel tube was heated in the muffle furnace (Nabertherm, Model L1/12/R6 to the desired temperature by using the heater under the heating rate of 10^{O}C/min. Biochar was put into the reactor at room temperature. Before heating, to avoid the possible oxidation of products, a small flux of inert gas by N_2 was introduced to the reactor to replace the air. The reactor was heated at the temperature of 400^{O}C, the reaction time of 20 minutes for cassava rhizome. Then, the biochar from cassava rhizome was analyzed following in section 1 and 2.

Scanning electron microscopy (SEM) images of the biochar produced from cassava rhizome was taken by a Jeol (JSM-6610LV). The liquid adsorption test, measuring the adsorption quality of the derived biochar, was evaluated in terms of iodine adsorption capacity (Iodine number) reflecting the surface area. The iodine adsorption test was under the guidelines of ASTM D4607-14. [5]

III. RESULTS AND DISCUSSION

Thermogravimetric analysis (TGA) was conducted to determine the thermal stability of cassava rhizome during thermal processing. Figure 1 shows TGA plots of cassava rhizome with weight losses (due to the release of volatile matters) and temperatures. At the temperature below 200^{O}C, moistures of both biomass had evaporated.

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It can however be observed that degradation occurred in the active pyrolysis zone at 200-400^{O}C for both biomass and the weight losses of both biomass occurred due to the decomposition of cellulose and hemicellulose. Above 400^{O}C, the reductions of both biomass weights were attributed to the decomposition of lignin. [6] Heating values, proximate analysis, and thermal analysis of cassava rhizome (presented by Table 2) will be discussed in this section.

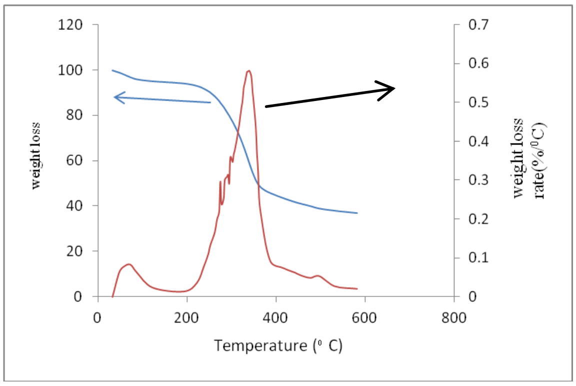


Fig1. TG-DTG curves of a) cassava rhizome b) corn on the cob

Table 2 shows the results of the proximate analysis of cassava rhizome before pyrolysis reaction (CR) and after the pyrolysis reaction (CRA). According to Table 2, in case of cassava rhizome, its moisture content decreased from 5.56% (CR) to 4.7% (CRA), fixed carbon rose from 18.91% (CR) to 65.35% (CRA), and ash content also increased from 6.54% (CR) to 11.25% (CRA). Nonetheless, the carbonization process caused sharp declines in volatile contents of both wastes, which were 58.17% for CR as opposed to 18.7% for CRA. Ashes after pyrolysis reaction of biomass increased from those of before pyrolysis reaction because the ratio of ash on the other components (fixed carbon, volatile matter, moisture content) rose corresponding with the increase of the fixed carbon and the decline of volatiles. Cassava rhizome, the heating value increased from 3,849 to 5,512 cal/g. After biomass sample was heated, the main solid remainder was fixed carbon, hence used to estimate the amount of yielded coke. [7]

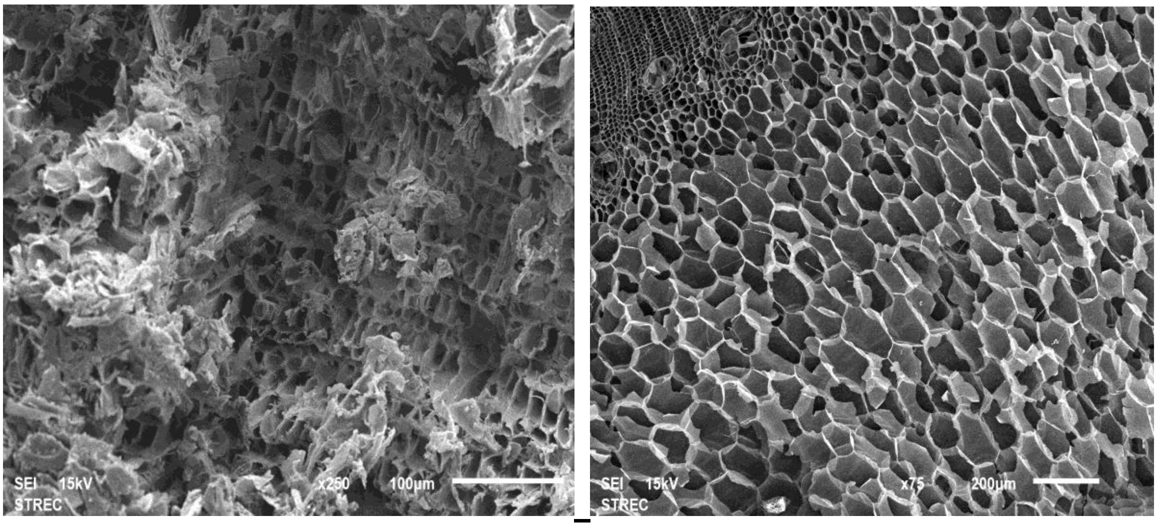
Table 2: Proximate analyses and heating values of cassava rhizome

Sample	Moisture (%)	VM (%)	FC (%)	Ash (%)	Heating value (Cal/g)
CR	5.56	58.17	18.91	6.54	3,849
CRA	4.7	18.7	65.35	11.25	5,512

Table 3: Ultimate analyses of cassava rhizome without pyrolysis (CR), cassava rhizome after pyrolysis (CRA).

Sample	C	H	N	O	H/C atomic ratio	O/C atomic ratio
CR	46.12	6.23	1.13	45.2	1.62	0.74
CRA	60.17	3.58	1.25	33.12	0.71	0.41

Table 3 indicates ultimate analyses and structural compositions of cassava rhizome before and after pyrolysis. The results show high contents of carbon and oxygen in CR due to lignocellulosic structures of agricultural residues. In addition, the content of cellulose is more than that of lignin for the biomass sample [6]. Chemically speaking, the molar ratio of hydrogen to carbon (H/C) is 1.67 for cellulose, $(C_6H_{10}O_5)_n$, and 1.6 for hemicellulose, $(C_5H_8O_4)_n$. In this respect, the molar ratio of H/C for cassava rhizome is around 1.62, indicating that the major organic components are cellulose and hemicellulose. Moreover, after the carbonization process CRA the molar ratio of hydrogen to carbon (H/C) are 0.71 and the molar ratio of oxygen to carbon are 0.41. Lignin has the lowest O/C atomic ratio close to 0.4 and it is rich in C=C in its aromatic ring as well as methoxyl ($-O-CH_3$) [7]. In contrast, CR had higher O/C atomic ratios due to higher cellulose content as CRA was pyrolyzed at the temperature of 400^0C. In fact, it is known that cellulose surface is rich in oxygenated groups, of which the typical functional groups are hydroxyl (-OH) and ether (C-O-C), resulting in increases in O/C atomic ratios. However, lignin is one of the most slowly decomposed components of dead plants, largely biodegrading into humus [8].



(a) **(b)**

Fig 2 (a) SEM image at 250X Magnification of cassava rhizome (CR), (b) SEM image at 75X Magnification of obtained biochar (CRA)

SEM analyses of CR and CRA at x 250 and x75 magnifications are illustrated in figure 2(a) and 2(b) respectively. Figure 2(a) shows an image of sample of porous yet shallow cavity while figure 2(b) is an SEM image of sample that has highly micro pores and a cavity suitable for adsorbing minerals, microbial habitat and soil enhancement in line with the results in Table 4 which shows iodine number of both biomass increasing from not adsorbed to 245 for cassava rhizome. It can be concluded that biochar produced from cassava rhizome has smaller pore volumes resulting in higher adsorption.

Table 4: Iodine NO. of Cassava rhizome

Sample	Iodine NO.
CR	Not adsorbed
CRA	245

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As there are increasingly alarming amounts of agricultural residues, especially cassava rhizome in the northeastern part of Thailand, air pollution has caused severe problems in the rural areas where farmers dispose of their agricultural wastes by means of incineration causing haze and more amount of wastes to the community. Based on the physical properties of cassava rhizome, and the findings derived from ultimate analysis and approximate analysis, it is safe to say that it is feasible to reduce the amount of cassava rhizome in the society by turning them into biochar manufactured on a large scale. Not only does it create a cost-effective energy output, but it also minimizes environmental problems. Special thanks go to Innovative Learning Center, Srinakharinwirot University for financial support to this study.

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