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EFFECT OF KOH CONCENTRATION ON MICROSTRUCTURE PROPERTY OF BIOCHAR FROM COCONUT SHELL BY LOW-TEMPERATURE PYROLYSIS

In this study, biochar derived from coconut shell biomass was synthesized by pyrolysis reaction with chemical activation using Potassium hydroxide (KOH). The biomass was carbonized by heating at low temperature 300°C for 3 hours with KOH content varied at 10 wt.%, 20 wt.%, and 30 wt.%. The effect of weight ratio between biomass and KOH on the characterization and structure of the biochar was investigated. An increase in the KOH content caused the change in the chemical composition and surface morphology of the biochar. The properties of raw material and biochar were examined by Xray fluorescence (XRF), scanning electron microscopy (SEM), and X-ray diffraction (XRD). When the content of KOH was changed in the range from 10 wt.% to 30 wt.%, the biochar had uniform porosity distribution with pore size around 0.5 µm and K_2CO_3 crystal equally distributed on the biochar surface. The synthesized biochar had porous structure with high Kali cation content, which was applicable for Kali rich fertilizer for soil amendment, adsorbent for heavy metals and carbon fuel in combustion processes.

Keyword: Coconut shell; biochar; pyrolysis; KOH; biomass

1. Introduction

Nowadays, biochar has gained significant scientific interest due to its diverse applications in environmental science, fuel production, and as an organic fertilizer. Recent publications highlight its use as an adsorbent for heavy metals and organic pollutants, a catalyst for biofuel production, a material for energy storage systems, an additive in cement manufacturing, and an amendment for soil fertilization [1]. Biochar has been shown to effectively adsorb heavy metals such as aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), uranium (U), and zinc (Zn) [2]. Additionally, biochar can interact with organic pollutants, adsorbing and removing substances from wastewater, including dyes, pesticides, herbicides, antibiotics, and other organic contaminants [3]. In Vietnam, coconut is ranked fourth among perennial industrial crops with a large planted area, after rubber, pepper, and cashew. Currently, the coconut area in the country is about 175,000 hectares, concentrated in the Central Coast provinces and the Mekong Delta. Coconut fruit from the Asia Pacific region, especially in Great Mekong Delta, Vietnam, are produced in large quantities and exported all over the world. Currently, global coconut production per year is 650,000 tons. More than 50% of the world's annual coconut shell production is used in developing countries.

Various research has shown that biochar can be produced from agricultural by-products such as corn stover [4], rice husk [5], sugarcane bagasse [6], coconut fiber [7], straw [8], sawdust [9], and so on. These biomass are often left on farms and then are burned, causing environmental matters such as global warming. Therefore producing biochar from agricultural residues contributes in reduction of green house gas emission. Various biomass feedstocks can be used to produce biochar, including wood and wood waste, agricultural residues, and other organic waste materials. In general, biochar is considered as a carbon-rich material, which has outstanding properties such as large specific surface area, high porosity density, a stable chemical structure and oxygen-containing surface functional groups. Biochar technology holds significant potential for addressing climate change, enhancing soil quality, reducing waste, and generating energy as a byproduct. Biochar is a form of charred organic matter created under high temperatures and low oxygen conditions, similar

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to those found in natural fires or modern pyrolysis systems. In such low-oxygen environments, biomass does not combust but instead decomposes through heat, resulting in a porous and stable form of organic material.

In terms of preparation of biochar, a popular method to derive carbon from biomass is pyrolysis, a thermochemical treatment in oxygen less environment. In this process, biomass decomposes into biochar under heat treatment with or without activation by catalyst. Common activators are chemical compounds such as $ZnCl_2$, Na_2CO_3, K_2CO_3, H_3PO_4, NaOH, KOH, $Ca(OH)_2$, and so on. After biomass was mixed with activators, the activation process was usually carried out at 300°C to 900°C. Activators ensured that the charcoal does not collapse in the pyrolysis and brought biochar a porous structure. The properties and potential applications of biochar are determined by the type of raw material and the specific production conditions. Additionally, coconut biochar, which was obtained from the pyrolysis of coconut shell at 700°C for 3.5 hours, had obtained the biochar [10]. However higher pyrolysis temperature up to 700°C prevent the main application in biochar industry. Thus, this research focus on reduce the pyrolysis by using binder activator. In this research, the biochar was synthesized from coconut shell by pyrolysis with KOH activator at low temperature as 300°C for 3 hour. The mass ratios between coconut shell and KOH were studied with the values of 0 wt.%, 10 wt.%, 20 wt.%, and 30 wt.% and investigate the microstructure changed due to the effect of KOH content. Based on the result finding, the research group can improve the biochar process for further industry application.

2. Materials and methods

2.1. Preparation of Coconut-derived biochar

Coconut shell was collected and dried under the sun for about 5-6 hours. Then, coconut shell was cut into small pieces. After being grinding, coconut shell powder was obtained. The coconut powder was sifted through a sieve with a diameter of less than or equal to 0.45 mm. After passing through the sieve, coconut powder was mixed with KOH and water and pressed into small pellets with 10 mm diameter.

The green coconut pellets were placed into the closing crucible and put in an oven for pyrolysis without oxygen environment. The carbonization took place at 300°C for 3 hours. Then the samples were cooled for post-pyrolysis processing. The flowchart process to produce coconut-derived biochar was given in Fig. 1.

2.2. Materials Characterization

The chemical composition analysis using Xray Fluorescence (XRF): the sample was characterized by Xray at 40 kV (ARL Advant, Thermo Scientific).

The phase analysis using powder-type and thin film XRD: the materials were ground and put in XRD machine (Bruker D8 Advance, Germany) with the 2theta scanning from 5 to 60-degree, operation at 40 kV and 40 mA.

The morphology analysis using SEM: the sample was scattered on Carbon tape stick to copper substrate and carried out by the SEM and EDX analysis (Hitachi S-4800) at 10 kV.

3. Results and discussions

3.1. Coconut Shell Raw Material Analysis

The chemical composition of raw coconut shell, as determined by XRF (X-Ray Fluorescence) analysis, is provided in TABLE 1. It appears that coconut shell has a high loss on ignition (LOI) value of around 97.3 wt.%. LOI represents the weight percentage of material lost when a sample is heated to high temperatures, typically indicating the presence of volatile organic compounds or moisture content. In the case of coconut shell, the high LOI value suggests the presence of a significant amount of cellulose, hemicellulose and a part of lignin which are major components of plant biomass. Cellulose is a complex carbohydrate that forms the structural component of plant cell walls and can contribute to the high energy calorific value of coconut shell upon burning in an oxygen-depleted atmosphere.

TABLE 1

Chemical compositions (wt.%) of ground coconut shell

Sample name	Chemical composition (wt.%)				
	SiO_2	CaO	Fe_2O_3	Al_2O_3	LOI
Coconut shell powder	1.65	0.02	0.57	0.45	97.3

Additionally, the chemical analysis reveals that silica (SiO_2) is the predominant remaining element in coconut shell, accounting for approximately 1.65 wt.%. This is likely due to the adsorption of SiO_2-containing materials from the fertilizers used during the growth of coconut shell. Silica is a common component in plant materials and can be derived from the soil or applied as a fertilizer. Understanding the chemical composition of coconut shell is essential for assessing its potential applications

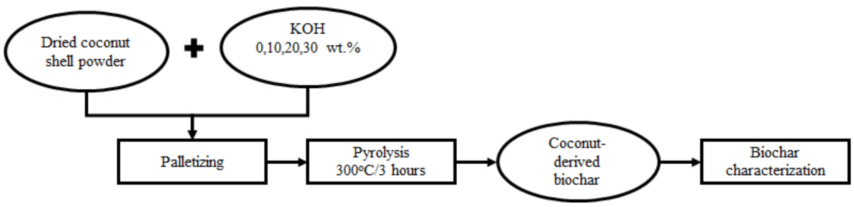

Fig. 1. Flowchart to produce coconut-derived biochar using coconut shell powder

and understanding its behavior during processing and conversion into activated carbon. The presence of high cellulose content and silica can influence the properties and characteristics of the resulting activated carbon, including its porosity, surface area, and adsorption capabilities. Beside the present of main SiO_2, the trace elenement of CaO, Fe_2O_3 and Al_2O_3 also found in coconut shell powder due to the uptake of these mineral from soil reulting in the hardness of coconut shell. Up to 97.3% of LOI indicating the high value of carbon content. As a result, coconut shell powder could be used as potential source of biochar due to its high carbon.

Fig. 2(a) illustrates the XRD pattern of the ground coconut shell as raw material. Basically, the main crystal phase of the raw material was Laumontite $CaAl_2Si_4O_{12}.4H_2O$ (PDF#26-1047) at 2theta = 21.5 degrees and 27.5 degree. Moreover, Fig. 2(b) describes the SEM image of coconut shell powder at a magnification of 2,000×. The morphology of coconut shell powder displays the aligned cellulose fibers with the pore size of 10 µm as show in white arrow. The cellulose wall can be deposited by the fiber as show by yellow arrow.

3.2. Characterization of Obtained Coconut-derived Biochar

Fig. 3 presents XRD patterns of coconut-derived biochar pyrolysis at 300°C for 3 hours with different amount of KOH activator binding (a) 0%; (b) 10%; (c) 20% and (d) 30%. As previously discussed, coconut shell is characterized by poor crystallization of SiO_2 and amorphous cellulose-containing carbon. Fig. 3(b) and (c) show XRD pattern of biochar after pyrolysis at 300°C for 3 hours with amount of KOH is 10 and 20%. The

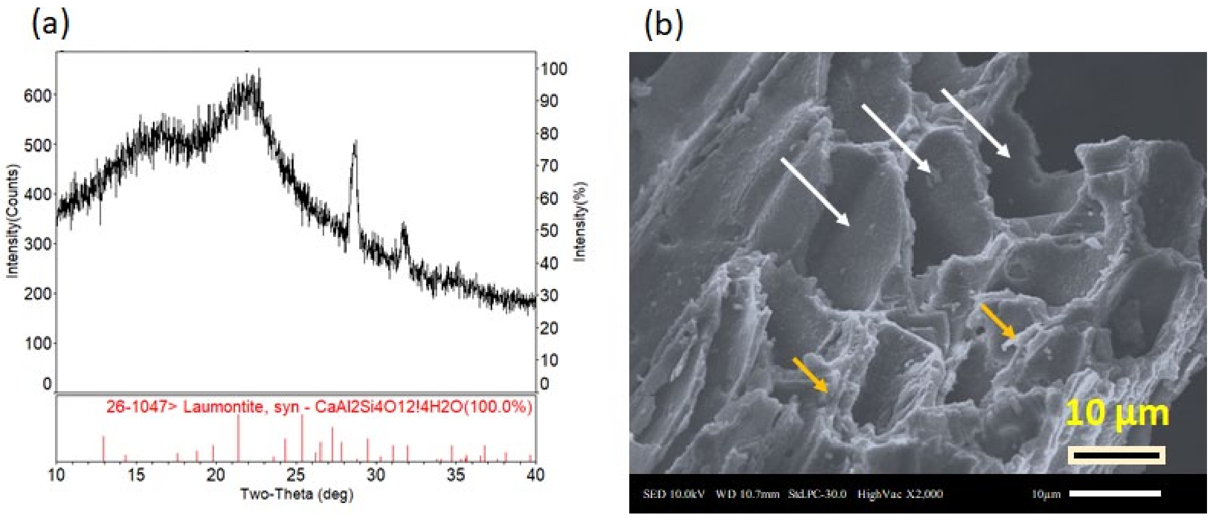

Fig. 2. XRD patterns of (a) coconut shell powder and (b) SEM image of coconut shell raw materials

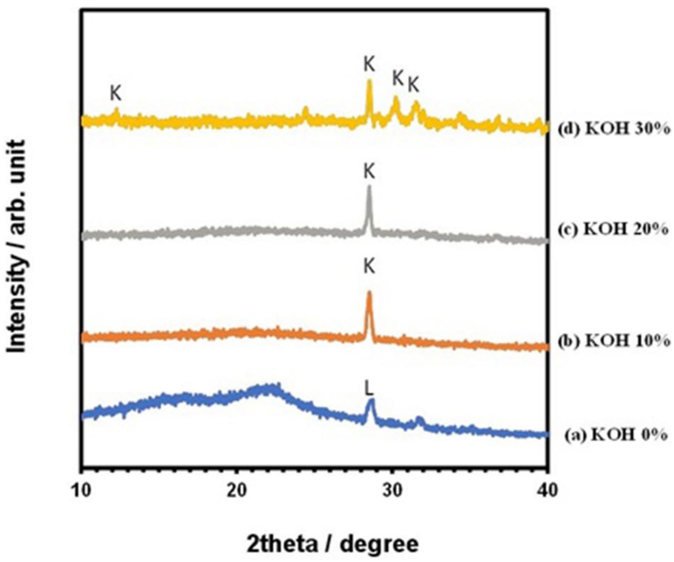

Fig. 3. XRD pattern of coconut-derived biochar pyrolysis at 300°C for 3 hours with different amount of KOH activator binding (a) 0%; (b) 10%; (c) 20% and (d) 30%. Code: L: Laumontite mineral $CaAl_2Si_4O12.4H_2O$ (PDF#26-1047); K: $K_2CO_31.5H_2O$ (PDF#11-0655)

peak of $K_2CO_3.1.5H_2O$ (PDF#11-0655) can be observed at 2theta of 28 degree. However, with the use of KOH binder up to 30%, the resulting sample exhibits the presence of $K_2CO_3.1.5H_2O$ (PDF#11-0655) is detected at 2theta angles of 13, 28, 31 and 32 degrees as show in Fig. 3(d) due to higer amount of KOH binding. The emergence of these peaks in the XRD pattern can be attributed to the chemical reactions occurring during pyrolysis, as described by Eq. (1). This equation may involve the interaction between potassium (K) and carbon (C), resulting in the formation of $K_2CO_31.5H_2O$. Further analysis and investigation are required to fully understand the details of the reaction and the role of $K_2CO_31.5H_2O$ in the overall process.

$$C + 6KOH \rightarrow 2K_2CO_31.5H_2O + 2K + 1.5H_2\ (gas) \quad (1)$$

Fig. 4 shows the SEM images of coconut shell derived biochar at magnification of 10,000×, which exhibits a vary morphology due to the change of KOH content. Upon pyrolysis with KOH at 300°C for 3 hours, small pore sizes are observed due to the evaporation of H_2 gas, as indicated by white arrow in Figs. 4b, 4c and 4d, The present of H_2 gas can be explain by

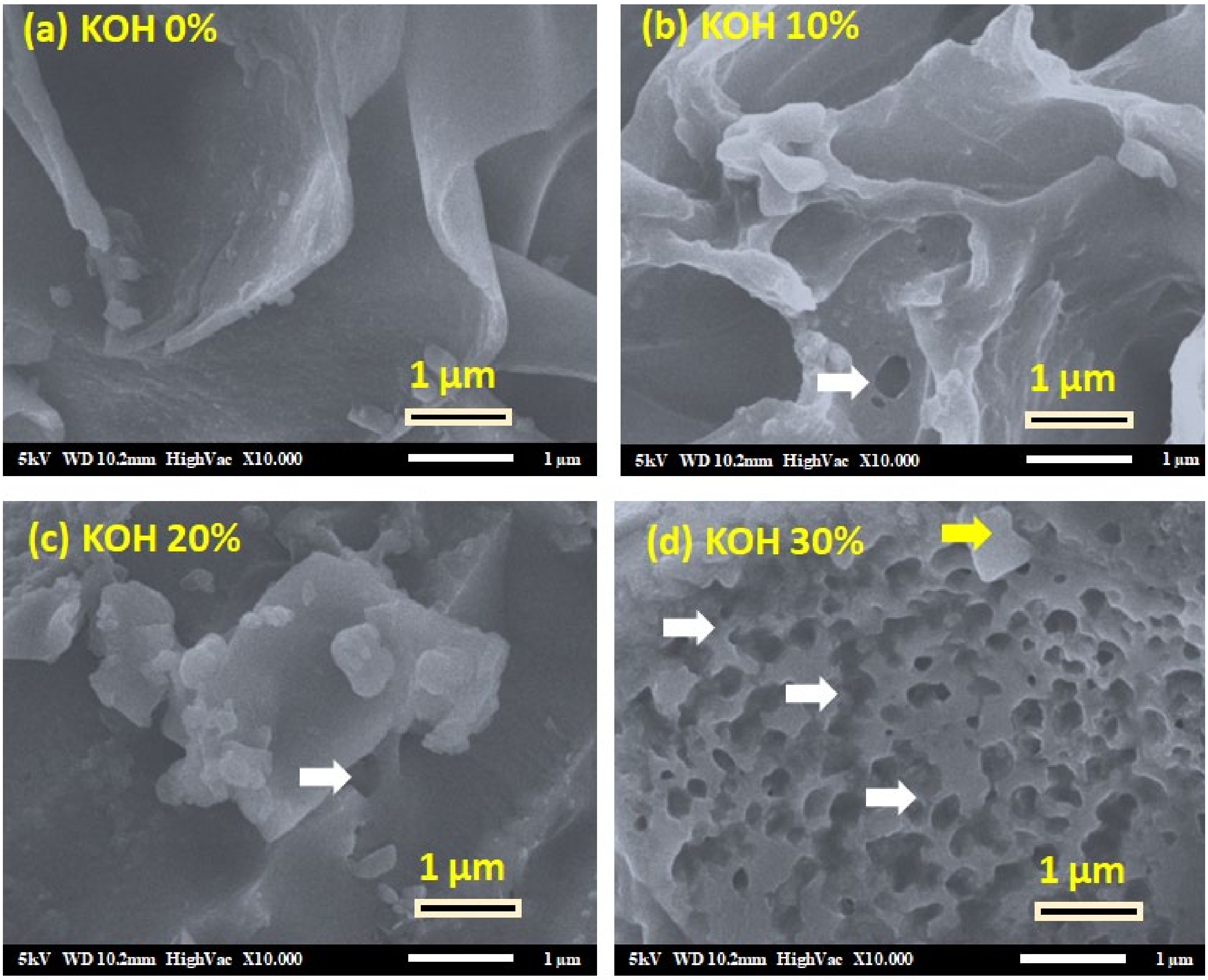

Fig. 4. SEM images of coconut shell derived biochar pyrolysis at 300°C for 3 hours at different content of KOH binding activator (a) KOH 0% at 10,000×; (b) KOH 10% at 10,000×; (c) KOH 20% at 10,000×; and (d) KOH 30% at 10,000×

Eq. (1). The resulting coconut shell-derived carbon possesses pores with pore size vary from 0.5 µm (as shown in Fig. 4d), suggesting its potential application in adsorbing heavy metals and serving as porous carbon fuel in combustion processes.

This research should be considered in the context of the experimental conditions and the potential applications of the findings. The main objective was to investigate the effect of KOH bonding on the formation of biochar using coconut shell as raw material. As mentioned in the introduction section, Coconut fruit from the Asia-Pacific region, particularly the Mekong Delta in Vietnam, is produced in large quantities and exported worldwide. Global coconut production currently stands at approximately 650,000 tons per year. Over 50% of the world's annual coconut shell output is utilized in developing countries. Currently, global coconut production per year is 650,000 tons. More than 50% of the world's annual coconut shell production is used in developing countries. The growing market demand for environmentally friendly products is something that coir should step into quickly. This is a gentle, soil-free planter made from fibers found between the coconut shell and the outer surface. Since it is a naturally produced material, it is completely renewable and is considered an excellent choice for environmental sustainability. Thus, our research group aim to use coconut shell as starting materials to supply carbon to form biochar. Previous result using coconut shell as starting materials, but require higher pyrolysis temperture such as 700°C [10] without using activator binding. Thus, our research group aim to use alkaline activator to reduce the pyrolysis temperature by chemical reaction between K from KOH and C from coconut cellulose. In this research, the content of KOH binding activator was investigated. Analysis of SEM data revealed that the activated biochar carbon obtained from this process exhibited a highly porous surface with an average pore size of ~0.5 µm upon using KOH content up to 30 wt.%. These results indicate that the activated carbon derived from coconut shell through the pyrolysis activation process could offer significant advantages in applications related to heavy metal removal or as a carbon-based fuel in industries such as soil water holding and adsorption capacity [11-14]. In addtion, biochar could be used thanks to its abundant surface functional groups due to its catalytic ability, electrical conductivity, and reactivity. Thus this research finding on the role of KOH cotnribute to the widen application of biochar in industry.

4. Conclusions

In this study, we explore the effect of KOH concentration on the microstucture change of coconut-dervied biochar using the pyrolysis activation process. The resulting biochar, with a pore size of approximately 0.5 μm increse with the increasing of KOH content up to 30 wt.%. This uniform porous biochar offers several potential applications, such as Solid Refuse Fuel (SRF), Catalyst Material, and Drug Materials. The nature porous structure of the biochar could allow for effective heavy metal adsorption. These applications might highlight the versatility and potential of the biochar fabricated from coconut shell, featuring a highly interconnected capillary porous structure. The material's properties, including its pore size and surface area, make it suitable for a range of uses, from energy generation to environmental and pharmaceutical applications.

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