

CHARACTERIZATION OF ACTIVATED BIOCHAR PREPARED FROM PINEAPPLE WASTE FOR METAL CATALYST SUPPORT

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Abstract

The utilization of agricultural residues for biochar processing has recently attracted attention due to the potential in many applications. One of the most urgent options for biochar is as a support material used in the catalytic process. In this study, activated biochar which has a high surface area and is inexpensive was prepared from pineapple waste mostly available in the southern and eastern parts of Thailand. The raw pineapple waste was previously carbonized at the desired temperature (400 and 600°C) using different heating rates (7 and 20°Cmin⁻¹) and steam was added immediately as an activator. The BET surface area was developed from 0.95 to 228.34 m²g⁻¹ by increasing the carbonization temperature with steam activation. A higher carbon percentage was also represented in a high-temperature condition. From the observed results, this new finding hints that the produced activated biochar from pineapple waste showed a beneficial characteristic which is available for use as a metal catalyst support or other functional materials.

Keywords: Activated biochar, pineapple waste, pyrolysis, steam

Introduction

Biochar has been extensively noted as are interesting options in energy and conducive to several applications in environmental utilization. In order to wholesale industries. The uses of biochar as effectively apply biochar to the catalytic either a biocatalyst or metal catalyst support process, biochar as a catalyst for biogas reform

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was studied, and it showed a high potential for CH_4 conversion at up to 81% (Muradov *et al.*, 2012). Some research works have focused on the environmental uses regarding removal of contaminants under various conditions by metallic nanoparticles supported on biochar (Angin *et al.*, 2013; Li *et al.*, 2017). Besides the catalyst for biodiesel production having been developed using a biochar-based material, there was also investigated, according to the recent literature, the possibility of showing that biochar has been successfully adapted for the conversion of biofuels and chemicals (Dehkoda *et al.*, 2010). As far as we know, biochar has been produced from many carbonaceous materials such as agricultural by-products, organic wastes, municipal solid wastes, etc.; hence, these raw feedstocks from local sources to develop biochar would be an alternative resource due to their availability, low- capital cost, and being eco- friendly materials (Bhandari *et al.*, 2014). However, most active metal catalysts are mainly supported on high surface areas with low interaction with the metal to enhance the catalyst performance. Additionally, high specific surface areas have deduced the aggregation of metal catalyst nanoparticles on the supporter surface which possibly implied to increase the active site of catalyst (Moussavi *et al.*, 2012). One of the techniques to enhance the biochar porosity is the activation that is used in activated carbon production. The 2 categories of activation are commonly known as physical activation and chemical activation. The difference between the 2 processes is as a result of the activating agents. The carbonized samples are conventionally activated by air, carbon dioxide, or steam in physical activation at a temperature range between 600 to 900°C. Conversely, chemical activation is carried out through using chemicals such as potassium hydroxide, zinc chloride, phosphoric acid, etc. for the activation (Borchard *et al.*, 2012).

Several studies of carbon materials such as biochar, activated carbon, and carbon nanotubes have completely explored the catalytic process because of their advantageous properties to promote metal catalysts due to their flexible feature during the reaction, the ability to

enhance porosity by the activation, and even the synthesis process (Saygili and Güzel, 2016). Typically, biochar can be produced through the pyrolysis of carbonaceous substances; therefore, there is a variety of alternative and interesting materials including feedstocks. In recent years, agricultural by- products, such as rapeseed cake (Ozcimen and Karaosmanoglu, 2004), paddy straw, bagasse (Lee *et al.*, 2013), and sunflower husk (Colantoni *et al.*, 2016) have been manufactured into biochar. Based on information from the United Nations Food and Agriculture Organization (FAO), reported by Medina and García in 2015, pineapple is 1 of the most economic plants with up to 1.2 billion tons produced in 5 counties comprising Thailand, Tanzania, Brazil, Costa Rica, and Indonesia. These countries account for a half of the total pineapple production in the world. After the pineapple processing, the solid by-products have been revealed approximately 26-35 % of fresh fruit weight (Bokl and Appah, 2014; Ahjhwaw, 2016). Regarding recent literature, there are no studies that have reported pineapple biochar as having been utilized as a metal catalyst support. Furthermore, some pineapple waste- derived biochar has a high nitrogen percentage due to the high numbers of proteins and enzymes contained in pineapple waste residues (Chang *et al.*, 2015). The nitrogen content in biochar and other porous carbon materials reveals an enhancement of the surface and electrochemical properties when utilized as a metal catalyst support. The activity of Pt/Ru catalysts supported on nitrogen-doped active carbon for enhanced methanol electro-oxidation has been investigated (Gang *et al.*, 2008).

The aims of this study were to evaluate the potential of pineapple waste to be converted into activated biochar as a metal catalyst support and investigate the positive properties of biochar that can be developed by using steam activation at a temperature range for biochar production. The effects of the carbonization conditions and steam activation on the physical and chemical properties of pineapple waste- derived activated biochar exposed its beneficial properties as a support

material for metal catalyst nanoparticles through proximate and ultimate analyses, the Brunauer-Emmett-Teller (BET) method, and scanning electron microscope (SEM), respectively.

Materials and Methods

Materials

Pineapple waste (PW), which was used as a raw precursor for activated biochar, was donated by a local processing mill in the eastern region of Thailand. Nitrogen with 99.99% purity was supplied by Praxair (Thailand) Co., Ltd., (Bangkok, Thailand) for the carbonization and activation of the PW. The raw precursor was pretreated by washing and drying in an electrical oven at 105°C for 24 hours, and the dried precursor was cut into pieces 5 mm or less (Borchard *et al.*, 2012). The chemical characteristics of the PW (proximate and ultimate analysis) were characterized via the standard method (Saygili and Güzel, 2016), as shown in Table 1.

Pineapple Waste Carbonization and Steam Activation

The activated biochar was produced in a horizontal rotary tubular furnace. Figure 1 displays the scheme of the reactor made from stainless steel. The work tube with a diameter of 45 mm and a length of 130 mm based on the Teflon rotors was driven by an analogue control unit. In order to improve the efficient mixing between the samples and the steam during the activation, a rotary tube furnace was applied. 10 g of the prepared samples were carbonized at 400 and 600°C at an approximately constant heating rate of 7°Cmin⁻¹ under nitrogen as the inert atmosphere. Once the samples had been

maintained for 60 minutes at the desired temperature to complete the removal of volatile substances, steam was provided at 0.5 mLmin⁻¹ to activate the biochar sample for 1 and 2 h in order to investigate the effective properties for a metal catalyst support. The PW biochars prepared from each condition are noted in Table 1. The PW400 and PW600 samples focused on the effect of the carbonization temperature without steam activation, whereas steam activation for the PW-derived biochar were studied on PW400S-1, PW400S-2, PW600S-2, respectively. The applied formula was used to calculate the biochar production yield (Colantoni *et al.*, 2016):

$$Y (\%) = m/m_0 \times 100,$$

where Y is the yield of the produced biochar (%), m is the mass of the produced biochar (g), and m₀ is the raw PW. For carbonization and activation, each experiment was completed 3 times. Hence, Y is the average value from the effective experiments.

Characterization of PW Derived Biochar and Its Activated Biochar

The characterization of the PW biochar and its activated biochar were completely characterized on chemical compositions by

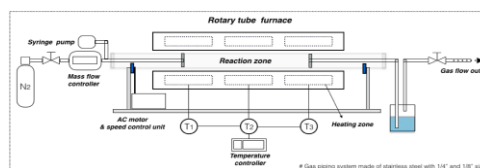


Figure 1. Scheme of rotary tube furnace for activated biochar production

Table 1. Conditions of pineapple waste derive biochar

Samples	Carbonization temperature (°C)	Hold time in steam activation (h)
PW400	400	-
PW400S-1	400	1
PW400S-2	400	2
PW600	600	-
PW600S-1	600	1
PW600S-2	600	2

proximate and ultimate analyses. Proximate and ultimate analyses have been done for both the raw materials and biochar samples. The proximate analysis was completed with a PerkinElmer Pyris 1 thermogravimetric analyzer, (PerkinElmer, Inc., Waltham, MA, USA); about 5 mg of each sample was heated from 30 to 900°C in nitrogen at a constant heating rate of 10°Cmin⁻¹ and then rapidly substituted to an oxygen surrounding, following the ASTM standard methods (i.e. ASTM D2867-99, ASTM D2866-94, ASTM D5832-98) to reveal the moisture, volatile matter, fixed carbon, and ash contents (Dizbay-Onat *et al.*, 2017).

In addition, the ultimate analysis that elucidates the percentages of carbon, hydrogen, and nitrogen was determined with a TrueSpec CHNS-628 CHN elemental analyzer (Leco Corp., St. Joseph, MI, USA), (Ormsby *et al.*, 2012). The surface morphology of the produced biochars was observed with a Zeiss EVO50 scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany) operating at 20 eV., while the pore structure of the PW

biochar and its activated biochar-conducted S_{BET} , V_T , and N_2 adsorption/ desorption isotherm were determined with a TriStar II 3020 gas adsorption analyzer (Micromeritics Instrument Corp., Norcross, GA, USA) using nitrogen operating at 77 K.

Results and Discussion

Thermal Property of Pineapple Waste and Biochar Yield

The important knowledge regarding the degradation characteristics of raw feedstock has been investigated since it may be indicative of the biochar production yield. The thermal behavior of the raw PW is displayed in Figure 2(a). The thermogravimetric (TG)/ differential thermogravity (DTG) analyses explain that the PW decomposition was focused on 2 main steps. The weight loss was greatly decreased below the temperature of 350°C because of the hemicellulose and extractive molecules in its structure at the first stage of the degradation. Secondly, the thermal behavior significantly exhibited that the degradation of the cellulose followed by lignin continuously occurred above 400°C. As seen in the DTG curve, the highest degradation rate was observed at the temperature range of 200 to 350°C according to hydroxyl deformation (Borchard *et al.*, 2012; Bhandari *et al.*, 2014). Figure 2(b) demonstrates the production yield of different PW biochars. Typically, the biochar yield was decreased with an increasing of the temperature at the carbonization stage due to the high deformation rate of the volatile substances (Ozcimen and Karaosmanoglu, 2004). Apparently, from the observations, the biochar yield was reduced from 36.41 to 25.02% with the PW400 and PW600 samples, respectively, whereas the results also showed that the biochar yield was obviously decreased after steam activation since the carbon atoms on the biochar matrix are transformed to carbon monoxide, carbon dioxide, and hydrogen which are products from the carbon steam reaction (Colantoni *et al.*, 2016). However, a lower yield may refer to its porosity. The lowest yield was obtained with

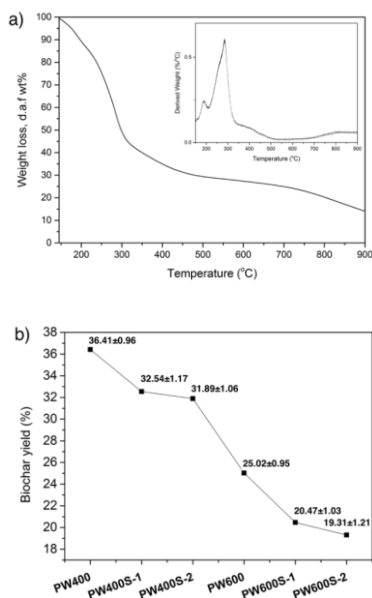


Figure 2. (a) TG and DTG curves of raw pineapple waste, and (b) biochar yield at different conditions

the PW600S-2 sample but it possibly produced the highest surface area, as seen in Table 3.

Proximate and Ultimate Analyses

The major parameters in the proximate analysis are the fixed carbon and ash contents since conventional biochar mainly consists of above 60% fixed carbon content and the promising properties of biochar played through these substances are such as energy density, adsorption capacity, etc. Previously, several studies revealed that the petty proportion of inorganic molecules in the biochar's structure might promote some catalytic reactions (Lee *et al.*, 2013; Colantoni *et al.*, 2016). The observations on the proximate analysis of the raw PW and its biochar are shown in Table 2. Seemingly, increasing the carbonization temperature powerfully influences the biochar's structure as is explained in PW400 and PW600. Both the fixed carbon and ash contents gradually elevated because of the released volatile substances from the PW structure, as the ash percentage was gradually elevated (Ormsby *et al.*, 2012). On the contrary, the highest fixed carbon was observed from

PW600S-2 at about 70.49%. The high fixed carbon possibly implies that biochar can have a high porosity. Beside the steam activation, the observations reported that the remaining volatile substances in the structure of the produced activated biochars (PW400S-1, PW400S-2, PW600S-1, and PW600S-2) were significantly reduced owing to oxidation with steam on the carbon surface establishing a higher fixed carbon percentage (Kastner *et al.*, 2012).

Ultimate analysis commonly illustrates the main elemental compositions of biochar (C, H, N, and O). The remaining nitrogen normally appears from the structure of raw feedstocks and probably was formed by chemisorption during the carbonization (Moussavi *et al.*, 2012; Dizbay-Onat *et al.*, 2017). From the elemental composition analyzed in Table 2, trace amount of nitrogen was found about 1.27 to 1.78 % that is greater than conventional biochar due to the high component of enzyme and proteins in pineapple structure (Bokl and Appah, 2014; Ahjhaw, 2016). The H content ranged from 2.45 to 4.26%. A large amount of C content

Table 2. Chemical and elemental analyses of PW raw feedstock and different PW biochars

Samples	Proximate analysis (d.b., wt%)			Ultimate analysis (d.a.f., wt%)			
	Fixed Carbon	Volatile Matter	Ash	C	H	N	O*
PW	9.65	87.14	3.37	41.73	7.61	1.27	49.39
PW400	45.91	46.34	7.75	69.30	4.26	1.78	24.66
PW400S-1	47.21	44.33	8.46	69.97	4.21	1.65	24.17
PW400S-2	48.73	42.96	8.31	70.13	4.14	1.68	24.05
PW600	68.74	21.21	9.55	79.48	2.53	1.53	16.62
PW600S-1	69.45	20.23	10.32	81.23	2.51	1.52	28.23
PW600S-2	70.49	19.84	9.67	81.78	2.45	1.47	27.45

*calculated by different

Table 3. Pore characteristic of different PW biochars

Property	PW400	PW400S-1	PW400S-2	PW600	PW600S-1	PW600S-2
S_{BET} (m^2g^{-1})	0.95	2.56	3.12	5.03	206.28	228.34
V_T (cm^3g^{-1})	0.0006	0.001	0.002	0.004	0.11	0.12

was found in PW600S-2 (81.78%). Certainly, the C content was enlarged with increasing the temperature at the carbonization step, and also with steam activation. From previous research, the direct proportion between the S_{BET} and C content has been investigated through its correlation (Kastner *et al.*, 2015; Dizbay-Onat *et al.*, 2017), as shown in Table 3.

Pore Structure Analyses

The S_{BET} and V_{T} of the produced biochars are presented in Table 3. PW400 and PW600 exhibit the effects of the temperature of the carbonization on the pore structure; according to PW600, the S_{BET} that was suddenly elevated from 0.95 to 5.03 m^2g^{-1} resulted from the enhancement of the biochar's porosity at the high-carbonization temperature with a high reduction of volatile substances in the carbon structure, as seen in Table 2, while the influence of the steam activation time is also shown in PW400S-1 and PW400S-2.

It shows the slight development of the porosity compared to PW400 since the carbon steam reaction occurs at a high temperature, which indicates that the endothermic reaction of gasification generally occurs above 600°C (Kastner *et al.*, 2015; Rajapaksha *et al.*, 2015). Next, the high S_{BET} shown in PW600S-1 and PW600S-2 are 206.28 and 228.34 m^2g^{-1} , respectively. The steam combined carbonization temperature at 600°C strongly develops the pore structure, although the high-carbonization

temperature has a strong influence on pore characteristics in steam activation, while the steam activation time also shows the effects on the pore structure of biochar as correlated to PW600S-1 and PW600S-2. The total pore volume (V_{T}) also increases unimportantly at a low-carbonization temperature even though the combined steam activation was due to the low release of volatile substances and limitation of the carbon steam reaction. Thus, the pore development is strongly connected to an increasing carbonization temperature combined with steam activation as shown in PW600S-1 and PW600S-2 at 0.11 and 0.12 cm^3g^{-1} , respectively.

The N_2 adsorption isotherm conventionally illustrates the pore characteristics of porous material analysis. Figure 3 displays the adsorption and desorption isotherms at 77 K of the activated biochar prepared from the condition of 600°C under steam atmosphere of 1 and 2 h, respectively. The characteristic of the isotherms identified the trend of the Type I and Type IV adsorption isotherms following the International Union of Pure and Applied Chemistry (Kastner *et al.*, 2015). The Type I and Type IV isotherms exhibited the characteristics of a micro/mesoporous structure. At a relative pressure below 0.2, the shape of the isotherms commonly indicate the micropore adsorption, whereas the widening hysteresis loop at a high relative pressure refers to the development of the mesoporous structure (Dizbay-Onat *et al.*, 2017). However, the isotherm of PW600S-1 is similar to PW600S-2, but the volume of adsorbed nitrogen is higher in the case of a greater holding time in the steam activation. For the pore size distribution, the result was demonstrated by using the Barrett-Joyner-Halenda model. The average pore sizes were approximately below 2.6 and 2.8 nm for PW600S-1 and PW600S-2, respectively. According to the pore analysis, the prepared activated biochars derived from PW is a possibility for the development of PW into a metal catalyst support because of the effects of pore development when using steam activation on high carbon composition and surface areas.

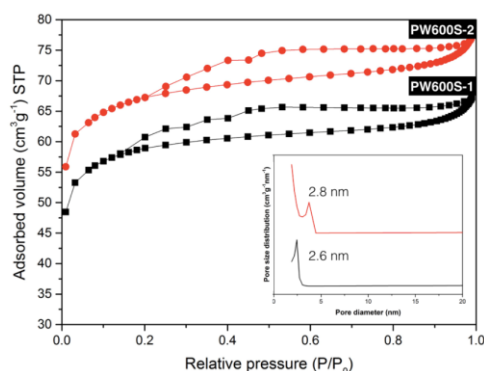


Figure 3. N_2 adsorption/ desorption isotherm of a) PW600S-1, and b) PW600S-2

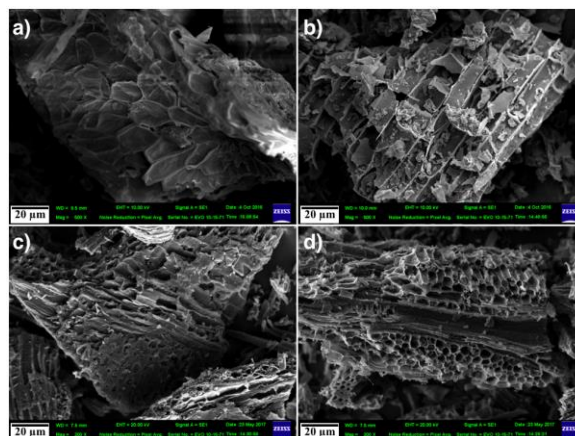


Figure 4. SEM images of a) pineapple waste, b) PW400, c) PW600, and d) PW600S-2

Surface Morphology of Pineapple Waste and Its Activated Biochar

The SEM micrograph of the PW and its biochar are shown in Figure 4. The PW exhibited a less porous, compact, and smooth surface morphology (Figure 4(a)), whereas Figure 4(b-c) shows the development of the pore structure with an elevated carbonization temperature on the microstructure of PW400 and PW600. The appearances showed various pores and cavities at a high- pyrolysis temperature causing higher degradation of volatile substances which effectively affects the formation of pores. Contrarily, PW600S-2 has various external pores on its surface structure as shown in Figure 4(d). The surface of PW600S-2 remained highly porous and the rough surface resulted from the carbon steam reaction in steam activation (Rajapaksha *et al.*, 2015). However, the pore structure analysis can ascertain the physical morphology of different PW biochars. From the results in Table 3, PW600S-2 reveals the highest BET surface area at about $228.34 \text{ m}^2\text{g}^{-1}$ that correlated with the highly porous surface, as seen in Figure 4(d).

Conclusions

The development of pineapple waste into activated biochar with steam activation

resulted in positive effects such as the enhanced porosity and C percentage of the biochar. Due to the observed varieties, the findings disclose that PW-activated biochar can have good potential for a metal catalyst support because of the alternative material, eco-friendliness, and cost-effective production compared with commercial activated carbon, alumina, and other supporting materials. The series of PW600S reveals the highest S_{BET} with 2 h of steam activation ($228.34 \text{ m}^2\text{g}^{-1}$). In contrast, the second preference condition of the PW activated biochar is the condition at 600°C under steam activation for 1 h due to the identical S_{BET} ($206.28 \text{ m}^2\text{g}^{-1}$), and the activated biochar produced under this condition significantly revealed a lower energy consumption. Thus, PW activated biochar could be applied as an alternative support material owing to its high percentage of C and high surface areas. However, the PW activated biochar should be further investigated on its efficiency as a metal catalyst support for utilization in the catalytic process.

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