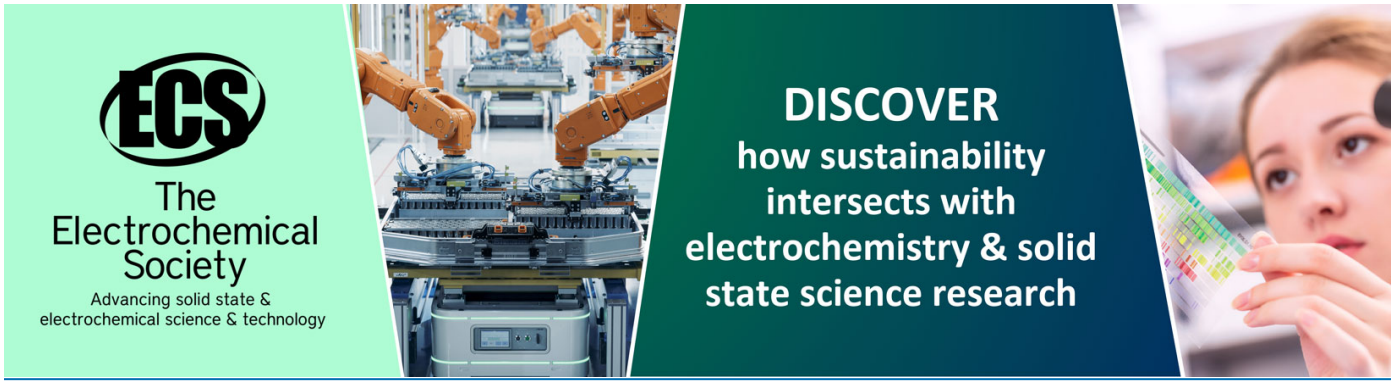
Production of activated carbon by using pyrolysis process in an ammonia atmosphere



IOP Conf. Series: Journal of Physics: Conf. Series **817** (2017) 012006 doi:10.1088/1742-6596/817/1/012006

Production of activated carbon by using pyrolysis process in an ammonia atmosphere

N Indayaningsih, F Destyorini, R I Purawiardi, D R Insiyanda and H Widodo

Research Center for Physics, Indonesian Institute of Sciences, Kawasan Puspiptek, Tangerang Selatan, Banten, Indonesia

Email: nani005@lipi.go.id; naniksih@gmail.com

Abstract. Activated carbon is materials that have wide applications, including supercapacitor materials, absorbent in chemical industry, and absorbent material in the chemical industry. This study has carried out for the manufacturing of activated carbon from inexpensive materials through efficient processes. Carbon material was made from coconut fibers through pyrolysis process at temperature of 650, 700, 750 and 800^{o}C. Aim of this study was to obtain carbon material that has a large surface area. Pyrolysis process is carried out in an inert atmosphere (N_2 gas) at a temperature of 450^{o}C for 30 minutes, followed by pyrolysis process in an ammonia atmosphere at 800^{o}C for 2 hours. The pyrolysis results showed that the etching process in ammonia is occurred; as it obtained some greater surface area when compared with the pyrolisis process in an atmosphere by inert gas only. The resulted activated carbon also showed to have good properties in surface area and total pore volume.

1. Introduction

Carbon is one of the materials that attracted most researchers' attention in recent decades, because it can be applied as smart materials. The development of technology enables the use of carbon for various applications, for instance electronic-textiles, super-capacitor, sensor, batteries [1, 2], biomedical [3], electrochemical devices, hydrogen storage, field emission devices, electronic devices [4], air, water and gas filtration [5, 6], conductive or reinforced plastics, structural composites, catalyst supports, and electrode fuel cell.

Carbon can be obtained from the decomposition of organic substances or biomass waste, such as coconut fibers, which is abundant and easily available. Decomposition process occurs usually by heating at a temperature corresponding to the thermodynamic conditions of the precursor to form charcoal, including by-products such as tar and gases. The process known as the carbonization or pyrolysis, conducted in the absence of air/oxygen [7] or in an inert gas condition [8, 9]. Nitrogen (N_2) or argon (Ar) gases are usually used in the pyrolysis process to obtain carbon [10]. The inert gas is a stable and non-reactive gas which causing the degradation of material without oxidation [11]. Form the references; it had conducted several ways to produce carbon with good characteristics in terms of high porosity and surface area [12-14]. Charcoal or carbon is then processed to form internal pores within the macro-, meso- and micro-pores in order to generate a larger surface area [15, 16].

Activated carbon has been extensively used as a material for energy storage due to large surface area, stable, easily polarized, amphoteric character, accessibility, relatively low cost and environmentally friendly [17]. It has been also used for filter of impurity elements [13] and as an

absorbent [18]. Super-capacitor based carbon is used as a constituent of the electrode material in order to produce a large surface area. The larger surface area required for storage of cargo in the form of electrolyte ions, this occurred during the charging process, ions are stored at the interface of electrode/electrolyte [19].

The activation process involves the physical mechanism by providing gas (gasification) or insertion of a chemical compound, also involves heating at relatively high temperatures [14, 16]. Chemical activation has the advantage, namely low temperature process to generate higher yields and could control at the micro level [20], chemical agent used such as phosphoric acid, zinc chloride, potassium hydroxide [13, 14, 21], and sodium hydroxide [22]. However, the use of chemical substance to increase the carbon characteristic is time consuming, costly and hazardous for the environment. The use of ammonia in pyrolysis process is a breakthrough to decrease the pollutions. Ammonia (NH_3) contains nitrogen and hydrogen atoms which are abundant in the earth [23]. The active carbon from cellulose filter has been made using the pyrolysis process in NH_3 atmosphere. The mechanism is leading to a process of gasification of carbon to form methane (CH_4), the etching process resulting in a larger surface area compared to pyrolysis in nitrogen [24].

In this study, activated carbon from coconut fibers had been made through the pyrolysis process in an atmosphere of ammonia at various temperatures, to observe the effect on surface area.

2. Material and methode

2.1. Preparation of active carbon materials

Coconut fibers as raw marerial were subjected to degumming process by immersion in a 10% NaOH (Merck) solution 90-95 ^{o}C temperature for 2-3 hours then washed, drained and dried. In this study, the weight ratio of fiber and NaOH is 1:5. The above procedure is aimed to obtain the cellulose and hemicellulose of coconut fiber. Through this step, it also will reduce the lignin and rubber that contained in coconut fiber [25]. The lignin and rubber will cause a sticky brown liquid during the pyrolysis process and affect the furnace.

Active carbon was made through a pyrolysis process with two step processes, including a carbonization followed by an activation steps. Carbonization process is carried out in an inert gas atmosphere (nitrogen gas) at a temperature of 450 ^{o}C for 30 minutes, followed by activation process in an ammonia (NH_3) atmosphere at various temperatures of 650, 700, 750 and 800^{o}C for 2 hours with a gas flow rate of 5 ml/min. The etching process is expected to occur during the pyrolysis process in an atmosphere of ammonia. This process is aimed to obtain a larger surface area and improve the properties of materials to produce activated carbon. Then, the carbon was grinded into powder for further sample characterizations.

2.2. Analysis and characterizations

An X-ray powder diffraction with a Cu tube anode an X-Ray Diffraction (XRD) Rigaku type SmartLab 3 kW was used to record the X-ray patterns of samples. Scanning electron microscopy (SEM from HITACHI SU-3500) and the samples Energy-dispersive spectroscopy (X-max, Horiba, Japan) probed at 4 points was used to visualize the surface morphology of the carbonized and activated products. The carbon content of these samples (charcoal that is produced) is also determined using scanning electron microscopy equipped with energy dispersive spectrometer. The EDS spectra showing elemental composition were obtained by scanning through the surfaces of the samples.

The surface areas measurements (m^2/g) of the activated carbon samples were made by low temperature nitrogen adsorption at range room temperature to 450^{o}C, 1^{o}C intervals, methods vacuum and flow on Brunauer Emmett Teller (BET) surface area analyser, by BET Nova 4200e with minimum pore volume 0.35-400 nm. The specific surface areas were estimated by the multipoint BET equation. The electrical conductivity was measured by using HIOKI 3522-50 LCR-meter.

3. Result and discussion

3.1. X-ray patternsof carbon

Microstructure of carbon in the charcoal of coconut fiber was analyzed using XRD. Figure 1 shows the diffraction spectra of the charcoal from coconut fiber prepared at temperatures of 650, 700, 750 and 800^{o}C. In XRD pattern, there are two main peaks with some slope slightly; this indicates that the carbon has an amorphous structure. The first peak of the carbon, as the result of pyrolysis process at of 600, 750, 750 and 800^{o}C, the 2-theta positions are 22.71, 23.65, 23.33, and 23.27^{o}, respectively. Increasing temperature of pyrolisis affect the shift peak position close to graphite peak position about 26^{o} [JCPDS PDF 75-2078]. EDS data also confirm that the dominant element is carbon, it also evidence some other impurities (Na, K, Si) however with amount less than 2 wt. %, as presented in tabel 1.

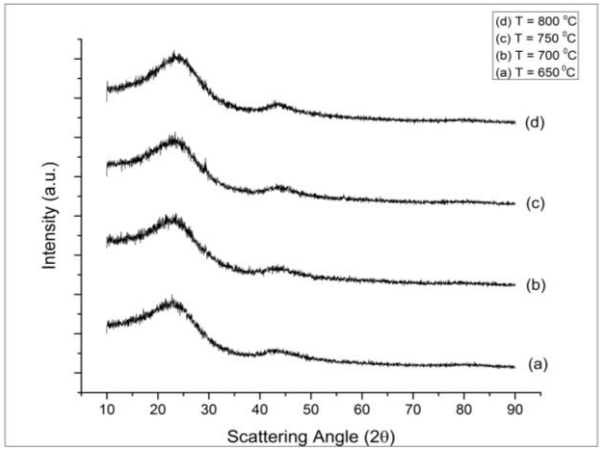


Figure 1. X-ray diffraction pattern of carbon prepared at variety of pyrolysis temperature.

Tabel 1. The EDS result of coconut fiber charcoal.

No	Element	%wt
1	C	85.68 ± 3.42
2	O	12.56 ± 2.97
3	Na	1.46 ± 0.49
4	K	0.25 ± 0.28
5	Si	0.14 ± 0.07

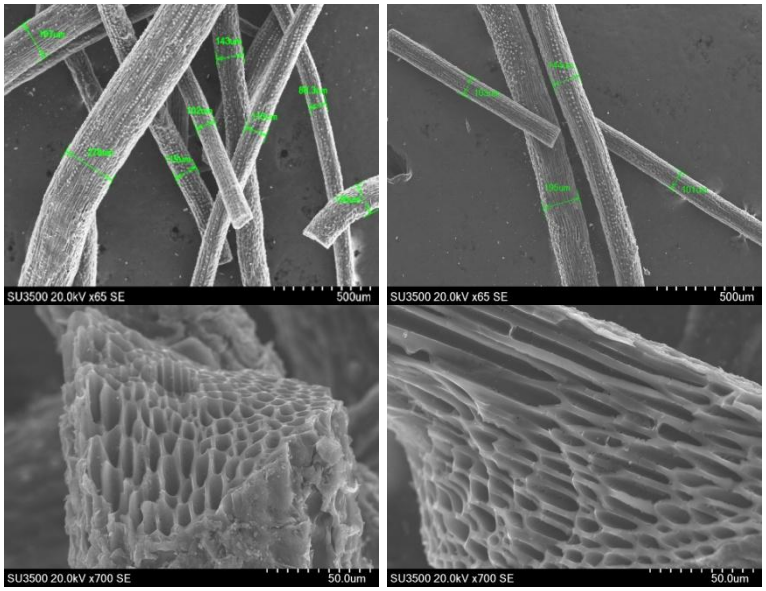
3.2. Surface morphology

The observation of carbon morphology using SEM is shown in figure 2 and 3. Hydrocarbon decomposition process on coconut fibers occurs during the pyrolysis in inert gas, and leaving the charcoal as by product. The morphology of charcoal is fibers shape with diameter of 100 –300 μm, consist of many parallel hollows like tube that are close to each other with diameters of 2 – 10 μm, and on the wall of the tube there are some porous with sizes around 1μm. The observations on carbon by pyrolysis results in an atmosphere of ammonia gas are presented in figure 3(b) and 4(b). The surface morphology showed finer than in nitrogen atmosphere. It seems some etching process on the surface of carbon is occurred, so the surface seems more tangled [24]. The elemental composition of carbon was also determined using scanning electron microscopy equipped with an energy dispersive spectrometer, the amount of carbon in the charcoal of coconut fiber was 85.68 ± 3.42 wt. %, the results showed that carbons are the dominant element in the charcoals.

3.3. Surface area analysis

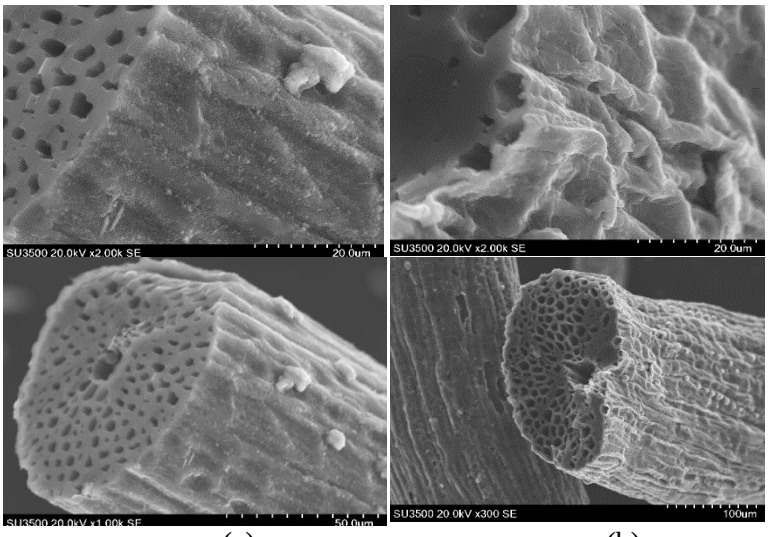
The observations and measurements using BET surface area indicates that the total pore volume of carbon increased with increasing pyrolysis temperature, as shown in figure 4(a). This suggests that the increase in temperature, causing the more volatile compounds disappear, consequently the greater pore volume is obtained. Initially, the pyrolysis temperature rise causes an increase in the average of pore radius of carbon and the average of pore radius dropped again for pyrolysis temperature at 800^{o}C, as

presented in figure 4(b). Average pore size at a temperature of 800^{o}C decreased, but the pore volume increases. This indicates that the degradation reaction continues during the pyrolysis process. Indeed, it does not add any large pore size; however it seems the number of new pores increase significantly. In observation of surface area, as presented in figure 5, the higher pyrolysis temperature, surface area rose in accordance with the total volume porosity.



(a) (b)

Figure 2. Surface morphology of carbon from coconut fiber with non-degumming process and pyrolysis process at atmosphere: (a) Nitrogen, (b) Ammonia.



(a) (b)

Figure 3. Surface morphology of carbon from coconut fiber with degumming process and pyrolysis process at atmosphere: (a) Nitrogen, (b) Ammonia.

3.4. Electrical conductivity

The results of the measurement of the electrical properties of carbon powder using an LCR-meter show that carbon is quite conductive, as shown in figure 6. Pyrolysis temperature increases, the higher the electrical conductivity. At temperature of 800^{o}C, electrical conductivity of carbon with ammonia gas treatment is slightly lower than the carbon with nitrogen gas atmosphere. This can be understood by observing on the SEM results (figures 2 and 3), which indicates that there is a change in morphology when linked with porosity. In the pyrolysis process using ammonia gas, giving the effect of etching on the surface of the sample, this led to an increase in porosity and surface area [26, 27]. From this result, the increase in porosity can give some effect on a decrease in the electrical properties.

The electrical conductivity of carbon is lower than graphite (output Fisher). It suggests that the electrical properties can be improved by raising the temperature pyrolysis.

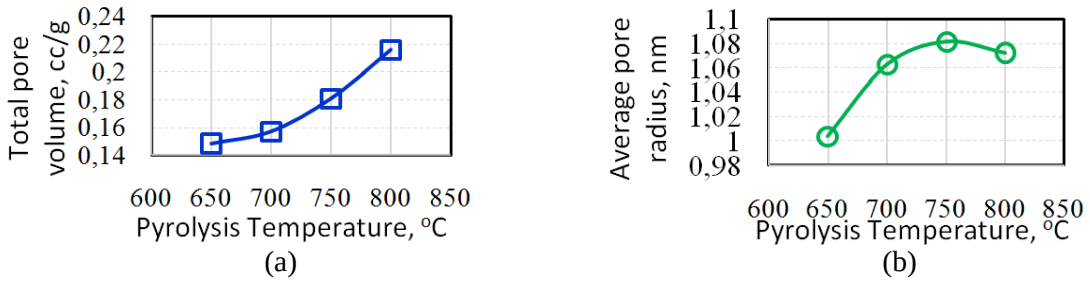


Figure 4. The total pore volume and average of radius pore of the carbon of coconut fiber with degumming process and pyrolysis process in ammonia gas.

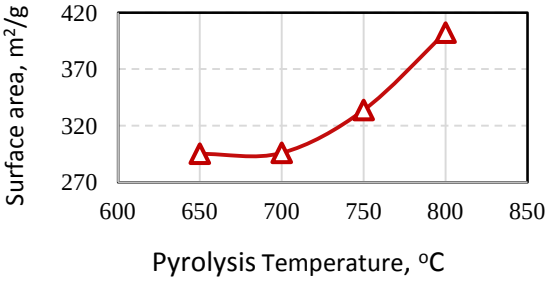


Figure 5. The surface area of coconut fiber carbon with degumming process and pyrolysis process in ammonia gas.

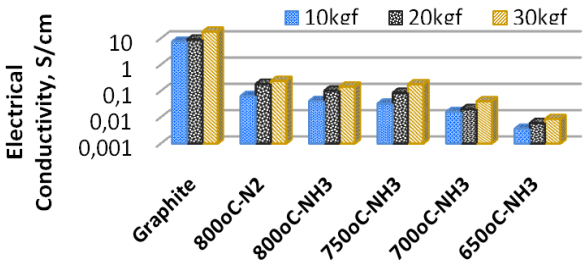


Figure 6. The electrical conductivity of thecarbon of coconut fiber with degumming process and pyrolysis process in ammonia gas.

4. Conclusions

In this study, activated carbon from coconut fibers have been made through the carbonization process in an inert gas and followed by pyrolysis process in an atmosphere of ammonia. Experimental data showed that the increase in temperature resulted in better properties of activated carbon. The activated carbon from coconut fibers is proven to have good properties in terms of surface area and total pore volume.

Acknowledgments

The authors gratefully acknowledge the financial support from Indonesian Institute of Sciences and the facilities provided by the Research Center for Physics—Indonesian Institute of Sciences.

References

[1] Dalton A B *et al* 2003 *Nature* **423** 703
[2] Baughman R H, Zakhidov A A and de Heer W A 2002 *Science* **297** 787-92
[3] Bianco A and Liu Z 2016 *Carbon* **97** 124-5
[4] Gehrke I, Geiser A and Somborn-Schulz A 2015 *Nanotechnol Sci. Appl.* **8** 1–17.
[5] Khajavi R, Bahadoran M M S, Bahador A and Khosravi A 2012 *J. Ind. Text.* **42** 219-30
[6] Fisher T, Hajaligol M, Waymack B and Kellogg D 2002 *J. Anal. Appl. Pyrolysis* **62** 331-49
[7] Vladimir K F, Vladimir A, Sinelshchikov, Sytchev G A and Zaichenko V M 2013 *Bionature 2013: The Fourth International Conference on Bioenvironment, Biodiversity and Renewable Energies (Lisbon)* (Wilmington: International Academy, Research and Industry Association) pp 29-32

[8] Ţiprigan O, Koos A A, Nemes - Incze P and Biro L P 2007 *Optoelectron. Adv. Mater. Rapid Commun.* **9** 617-20
[9] Health and Safety Executive 2011 *Using Electric Storage Batteries Safely* 1st edition (London: Health and Safety Executive Books) pp 1-10
[10] Saragih S A 2008 *Pembuatan dan karakterisasi karbon aktif dari batubara riau sebagai absorben* Master Thesis (Indonesia University) pp 11-2
[11] Ali E, Taherehand K S and Mansooreh 2011 *Res. J. Chem. Environ* **15** 433-7
[12] Rahman M M, Awang M, Mohosina B S, Kamaruzzaman B Y, Wan Nik W B and Adnan C M C 2012 *APCBEE Procedia* **1** 293-8
[13] Rashidi N A, Yusup S, Ahmad M M, Mohamed N M and Hameed B H 2012 *APCBEE Procedia* **3** 84-92
[14] Zhang M, He C, Liu E, Zhu S, Shi C, Li J, Li Q and Zhao N 2015 *J. Phys. Chem. C* **119** 21810-7
[15] Herawan S G, Hadi M S, Ayob Md R and Putra A 2013 *The Scientific World Journal* **2013** 1-6
[16] Frackowiak E and Be´guin F 2001 *Carbon* **39** 937-50
[17] Ilomuanya M O, Nashiru B, Ifudu N D and Igwilo C I 2016 *Journal of Microscopy and Ultrastructure* (In Press, available online 12 May 2016)
[18] Raymundo-Piñero E, Kierzek K, Machnikowski J and Béguin F 2006 *Carbon* **44** 2498-507
[19] Lillo-Ródenas M A, Cazorla-Amorós D and Linares-Solano A 2003 *Carbon* **41** 267-75
[20] Pandolfo A G and Hollenkamp A F 2006 *J. Power Sources* **157** 11-27
[21] Xu B, Chen Y, Wei G, Cao G, Zhang H and Yang Y 2010 *Mater. Chem. Phys*.**124** 504-9
[22] Roney N, Llados F, Little S S and Knaebel D B 2004 *Toxicologcal Profile for Ammonia* (Atlanta: Agency for Toxic Substances and Disease Registry)
[23] Luo W, Wang B, Heron C G, Allen M J, Morre J, Maier C S, Stickle W F and Ji X 2014 *Nano Letters* **14** 2225-9
[24] Mathew S and Zakaria Z A 2015 *Appl. Microbiol. Biotechnol.* **99** 611-22
[25] Liu L, Yang Q and Shen J 2015 *Journal of Nanomaterials* **2015** 1-9
[26] Han C, Kim I T, Sun H J, Park G, Lee J J, Lee H K and Shim J 2012 *Int. J. Electrochem. Sci*.**7** 8627-36