

Hydrogen Adsorption Capacity Reduction of Activated Carbon Produced from Indonesia Low Rank Coal by Pelletizing

(Pengurangan Kapasiti Penjerapan Hidrogen Karbon Aktifan melalui Pelet Dhasilkan daripada Arang Batu Kelas Rendah Indonesia)

SRI HARJANTO*, LATIFA N. NOVIANA, MIA DINIATI, STEFANNO W. YUNIOR & NASRUDDIN

ABSTRACT

Coal-based activated carbon materials is a prospective materials for hydrogen storage application. The present work aimed to study the effect of post treatments including mechanical milling process and pelletization and simulating experimentally the conditions of pelletization of fine particles of activated coal. Post treatment of activated coal consist of 2 steps mechanical milling process in planetary ball mill followed by pelletization. First step of mechanical milling process gave particle size reduction and second step was undertaken to maintain activity of activated coal. Second step of mechanochemical process were done in dry (ACP-A) and wet condition (ACP-B) with the ratio of sample: KOH was 1:1 and performed for 1 h. Then they will be formed into pellets with the addition of binder which contained fructose, glucose and oligo. Some examinations such as PSA, BET, SEM and XRD were performed to determine the characteristics of activated carbon materials including hydrogen adsorption capacity testing. Particle size reduction of activated carbon reached 98.9% after planetary ball milling. The raw material of activated carbon (AC) has hydrogen adsorption as much as from 0.30 and 0.25 wt. % from -5 and 25°C measurements, respectively. As predicted the adsorption of hydrogen gas of pelletized activated carbon from bituminous coal decreased due to post treatment process about 47% for ACP-A and 60% for ACP-B at 4000 Bar.

Keywords: Activated coal; bituminous coal; hydrogen adsorption; pelletizing; planetary ball mill; volumetric adsorption

ABSTRAK

Bahan berasaskan arang batu karbon aktifan adalah bahan prospektif untuk penyimpanan hidrogen. Kertas ini bertujuan untuk mengkaji kesan selepas rawatan termasuk proses pengilangan mekanik dan membuat pelet serta mensimulasi uji kaji keadaan membuat pelet daripada zarah halus arang batu aktifan. Pasca rawatan arang batu aktifan terdiri daripada 2 langkah proses pengilangan mekanik di kilang planet bebola diikuti dengan membuat pelet. Langkah pertama proses pengilangan mekanik ialah mengurangkan saiz zarah dan langkah kedua diambil untuk mengekalkan aktiviti arang batu aktifan. Langkah kedua proses kimia mekanik dijalankan dalam keadaan kering (ACP-A) dan basah (ACP-B) dengan nisbah sampel: KOH ialah 1:1 selama 1 jam. Kemudian mereka akan dibentuk menjadi pelet dengan pengikat yang mengandungi fruktosa, glukosa dan oligo. Beberapa ujian seperti PSA, BET, SEM dan XRD telah dijalankan untuk menentukan ciri bahan karbon aktifan termasuk ujian kapasiti penjerapan hidrogen. Pengurangan saiz partikel karbon aktifan mencapai 98.9% selepas pengisaran planet bebola. Bahan mentah karbon aktifan (AC) mempunyai pengukuran penjerapan hidrogen masing-masing sebanyak 0.30 dan 0.25 wt. % dari -5 dan 25°C. Seperti diramalkan penjerapan gas hidrogen daripada pembuatan pelet karbon aktifan daripada arang batu berbitumen menurun kerana proses pasca rawatan sebanyak 47% untuk ACP-A dan 60% untuk ACP-B pada 4000 Bar.

Kata kunci: Arang batu aktifan; arang batu berbitumen; membuat pelet; penjerapan hidrogen; pengisaran planet bebola; penjerapan isi padu metrik

INTRODUCTION

Activated carbon materials from various types of raw materials such as coal, coconut shells, wood and lignite are interesting choices for hydrogen storage media due to their porous structure and high porosity, high surface area, adsorption capacity, low density and relatively inexpensive (Jiménez et al. 2010; Ströbel et al. 2006; Wang et al. 2009; Yurum et al. 2009). It has specific surface area from 50 to 2000 m²/g and a variety of pore structures such as

micropores (<2 nm), mesopores (2-50 nm) and macropores (>50 nm) (Ahmadpour & Do 1996).

In Indonesia, low rank coal with calorific value less than 5100 cal/g is about 36% of coal reserves (Sihite 2012). Mainly, it is utilized as power plant fuel. Utilization of activated coal as hydrogen storage was investigated in previous studies, but none of them from Indonesia low rank coal (Fierro et al. 2010; Kopac & Toprak 2007; Tellez-Jua´rez et al. 2014; Ubago-Perez et al. 2006). These studies

showed that activated carbon from coal is a potential candidate for hydrogen storage materials application. It may diverse the utilization of low rank coal.

In general, higher surface area is needed for higher hydrogen adsorption capacity. Typically, it can be achieved by reducing their size in the range of micrometer and submicrometer-sized particles. However, materials handling of very fines particles is limited for hydrogen storage application. Therefore, this study aimed to evaluate post treatments such as pelletizing process of milled activated bituminous coal particles for hydrogen storage. Surface area, pore diameter, pore volume and pore distribution of sample after treatment which will affect the capacity of hydrogen adsorption were also examined. This study also compared the hydrogen adsorption capacity of activated coal samples with and without post-treatment by using volumetric method.

MATERIALS AND METHODS

MATERIALS

Raw material used in this study was commercial low rank activated coal from Indonesia in the form of granule with the average size of 38.8 μm (AC). The activation process of the raw material was carried out by physical-thermal activation. HCl solution 5 M was utilized as washing and rinsing solution to neutralize excess KOH in activated coal. Proximate analysis of the materials is shown in Table 1. It can be classified as bituminous coal.

TREATMENT PROCEDURE

Mechanical milling by mean of ball-milling method was employed to obtain fines particles of activated bituminous coal in micron and submicron size. The first step milling was conducted in a Planetary Ball Milling or PBM (NQM series – 4) for 30 h with the revolution speed of 300 rpm at room temperature (AC milled). Further mechanochemical process in dry and wet condition by using KOH as additional agent was undertaken. It was called as second stage milling aiming to promote mechanochemical reaction of the mixture. In case of dry mechanochemical process, milling process was conducted in dry condition without addition of water. The samples were mixed with KOH solid and the ratio of sample: KOH was 1:1. The speed of PBM was 200 rpm for 1 h (ACP-A). In case of wet mechanochemical process, milling process was undertaken by addition of KOH solution in water 50%. The milling was carried out for 1 h with a ratio of KOH to sample was 1:1 and the speed of PBM was

200 rpm (ACP-B). The ratio of steel ball to sample for all type of samples (ACP-A and ACP-B) was 1:5.

After mechanochemical process, the samples were washed and rinsed with 5M HCl and distilled water and dried for 1 h at 110°C. The next stage was pelletization on the dried sample by using a binder with the composition of binder are fructose, glucose and oligo by compacting the samples to cylinder form (5 mm diameter \times 10 mm length) and followed by drying the samples again for 2 h at 110°C.

CHARACTERIZATIONS

Particle Size Analysis (PSA, Delsa Nano, Beckman Coulter) test was conducted to determine the particle size of activated carbon before and after mechanochemical process. Activated carbon before and after mechanochemical processes were characterized by X-Ray Diffraction (XRD, Shimadzu XRD-7000 MAXIMA) for knowing the crystallinity of samples. Then, Scanning Electron Microscopy (SEM, LEO series 420-41-02) was conducted to observe the morphology of activated carbon before and after mechanochemical process. The surface area, pore diameter and pores volume of activated carbon before and after mechanochemical process were determined by Brunauer Emmet Teller (BET) test which used Novawin2-Acquisition Data and Reduction for NOVA Instruments 1004-2003.

The hydrogen storage capacity of activated carbon after mechanochemical process and raw material were determined by the volumetric adsorption test by measuring the pressure drop resulting from adsorption after exposing the sample to hydrogen at constant volume (Blackman et al. 2006). The volumetric adsorption test was performed at different temperatures (i.e. -5 and 25°C). The adsorption process was also done with variety of pressures of 250, 500, 1000, 1500, 2000, 3000 and 4000 kPa for each temperature. The hydrogen adsorption capacity apparatus employed in this study was similar with the previous study (Harjanto et al. 2013).

RESULTS AND DISCUSSION

PARTICLES CHARACTERISTIC AND MICROSTRUCTURE

Submicrons size particles were produced after mechanical milling for 30 h with the average particle size of 415 nm from 38.8 μm , the average size of raw materials (AC). Size reduction occurred due to the deformation and destruction of solids during milling, when steel balls

TABLE 1. Proximat analysis of activated coal

Sample	Moisture content (%, ADB)	Ash content (%, ADB)	Fly ash content (%, ADB)	Fixed carbon content (%, ADB)	Total sulfur content (%, ADB)	Calorie value (Cal/g, ADB)
Activated coal	21.1	10.9	6.6	61.3	0.63	5068

ADB: Air Dried Base

and the material within a jar was collided with each other so that the material will break down into smaller sizes. Qualitatively, Figure 1(a) shows AC with granule form. Macropores are observed in many location on the surface. Figure 1(b) illustrates milled AC particles which shows finer particles as product of comminution process during milling.

Figure 1(c) and 1(d) show the microstructures with different resolution of pelletized ACP-A which has been treated by dry mechanochemical and pelletizing process. The microstructure of pellet surface of ACP-A in Figure 1(c) illustrates relatively homogeneous particles size distribution that agglomerated in the pellet. More detail figure of the pellet microstructure is shown in Figure 1(d). There are some pores (macro pores), which still present on the surface of ACP-A. Mesopores and nanopores cannot be observed from the figures due to limitation of SEM resolution. Considering the location of macropores identified in the Figure 1(d), it is likely that they were formed during agglomeration and drying process.

Figure 1(e) and 1(f) shows ACP-B pellet microstructures which has been undergone wet mechanochemical and pelletizing process. It is shown in Figure 1(e), that some bigger particles were not perfectly reduced their size and were agglomerated with finer particles. The macro pores are also observed in many location on the ACP-B microstructures. Qualitatively, the amount of macro pores of ACP-B are many more than those of ACP-A. It

indicates that wet mechanochemical process followed by agglomeration process may produce less dense pellet than those of dry mechanochemical process.

SUBSTANCES BEFORE AND AFTER TREATMENTS

XRD patterns of the substances of activated carbon based on coal as raw materials and after treatment materials are shown in Figure 2. Peaks of carbon as major element are detected for raw materials activated carbon. Silica is also detected, since ash still presents in the materials. After first stage of milling treatment for 30 h, the crystallinity of carbon materials decreased with the decreasing of major peak of carbon. Further milling process aiming to mechanochemical process tends to transform carbon materials as amorphous. However, additional materials in the mixture i.e. KOH produces K_2CO_3 , by the reaction $2KOH + C + O_2 = K_2CO_3 + H_2O$ (1). KCl was also observed in the materials as excess salt from cleaning process. Prior to XRD examination, the materials were washed and rinsed by using HCl solution and distilled water. Actually, dry or wet mechanochemical process of activated carbon lead to the formation of amorphous materials. However, by comparing both process, it is clear that dry mechanochemical process (ACP-A) also produce other additional substance i.e. K_2CO_3 which is not identified in ACP-B. KCl with better crystallinity is observed from x ray diffraction peaks of ACP-B.

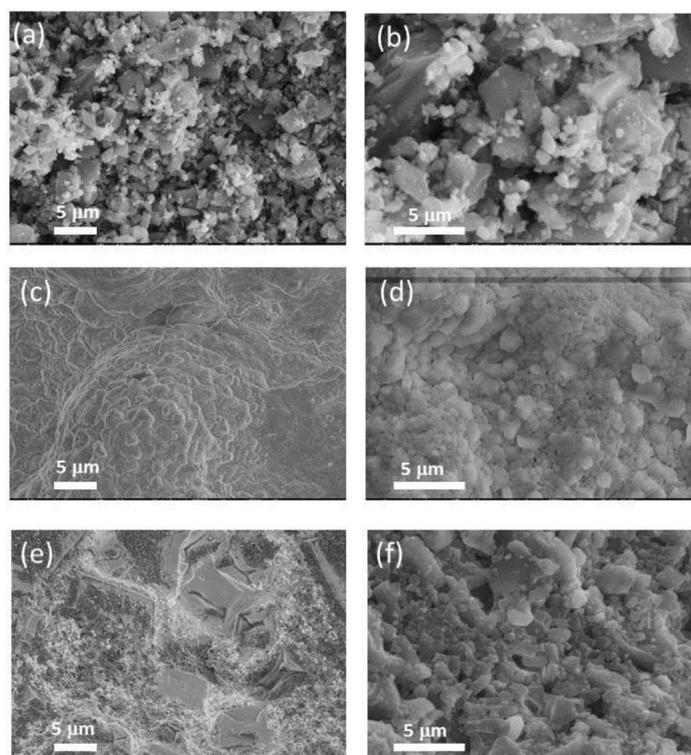


FIGURE 1. Microstructures of particles (a) raw materials, granule activated coal, (b) milled, (c) dry mechanochemical process followed by pelletization, ACP-A, (d) ACP-A in higher resolution, (e) wet mechanochemical process followed by pelletization, ACP-B and (f) ACP-B in higher resolution

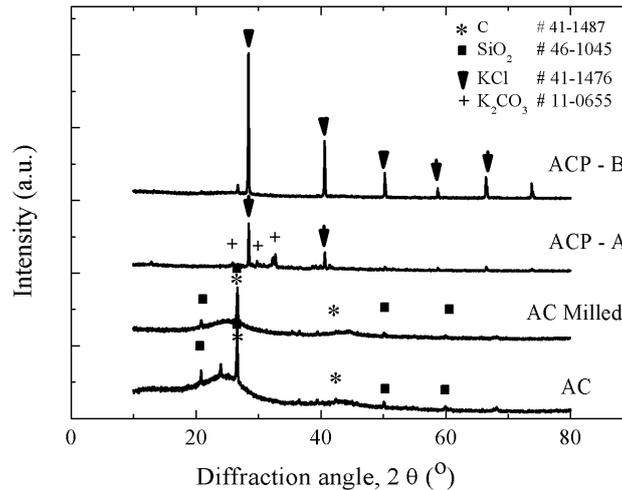


FIGURE 2. X ray diffraction (XRD) pattern of activated carbon based on coal before and after treatments

SURFACE AREA, PORE DIAMETER AND PORE VOLUME

The surface area of activated carbon as raw materials and after treatments is illustrated in Figure 3. Surface area reduction after milling (PBM) for 30 h was about 7%. This is due to PBM gave compaction effect on the activated carbon resulting in the destruction of porosity shape. The formation of new surface of particles which is relatively free of porosity is likely to occur. It can be observed and compared between Figure 1(a) raw materials (AC) and Figure 1(b) after first stage milling process. Figure 1(b) depicts the microstructure of milled AC which shows relatively clean surface of particles compared with those of Figure 1(a). It seems that the formation of new surface during milling process destroy the previous pore present in AC.

In case of ACP-A, the decrease of surface area becomes very significant and lower than that of ACP-B. As also shown in Figure 1(c) and 1(d), ACP-A looks denser with closed connection among particles than that of ACP-B. It means that pelletization from wet mechanochemical process materials

still give better surface area. The microstructures of ACP-A and ACP-B also confirm that the addition of binder affected to decreasing the surface area of AC.

Pore diameter and pore volume of activated carbon based on coal materials before and after treatments are shown in Figure 4. Original pore of AC from activation process was likely destroyed due to particle-particle and particle-ball impact during milling. Milling of AC may produce decreasing pore diameter and volume. The range of pore diameter is in between 2 and 3 nm. It is still categorized as mesoporous. Dry mechanochemical followed by pelletization gives smallest pore diameter. Mechanochemical process without addition of water gives more severe comminution effect on particles. Further treatments of AC by dry and wet mechanochemical followed by pelletization lead also in reduction of pore volume. Comparing the data of surface area, pore volume, pore diameter and assuming the porosity shape is like cylinder, treatments of AC i.e. mechanochemical process and pelletizing, tend to reduce its height or length

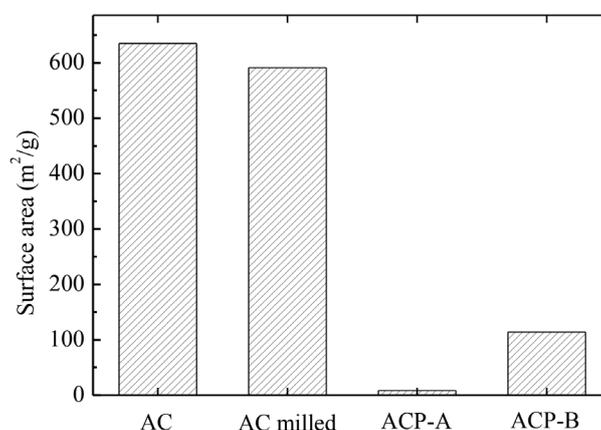


FIGURE 3. Surface area of activated coal before and after treatments

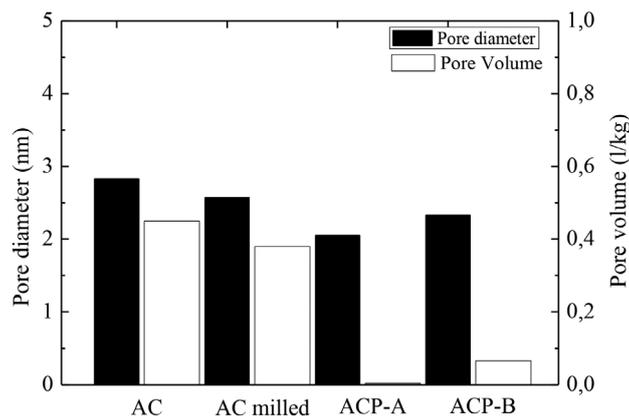


FIGURE 4. Pore diameter and pore volume of AC and treated activated carbon

significantly, because the pore diameter decreases slightly. Figure 4 also shows that dry mechanochemical and pelletization (ACP-A) gives lower pore volume than those of ACP-B. It indicates that dry mechanochemical process followed by pelletization effectively reduces pore volume of AC.

Raw materials of AC had pore volume of 0.45 L/kg. Milling of AC decrease in pore volume at 0.38 L/kg or only 45% pore volume capacity of AC. Mechanochemical process in dry condition (ACP-A) followed by pelletization gives the pore volume of 0.0043 L/kg or 0.1% of the pore volume capacity of AC. In case of ACP-B, post treatments decrease in pore volume of ACP-B at 0.066 L/kg or 15% pore volume of AC. It also suggested that treatments of AC, i.e. combination of mechanochemical and pelletizing may cause the decrease of the pore volume of AC, for instance, due to partial blocking of the pore by application of binder and/or destruction of pore shape. However, dry mechanochemical process lead to higher reduction of pore volume as shown in ACP-A than that of ACP-B.

HYDROGEN ADSORPTION CAPACITY

Figure 5 shows the comparison of the hydrogen adsorption capacity of activated carbon before and after post treatments at different temperatures. In general, the adsorption capacity of hydrogen will increase with increasing pressure and decreasing temperature. The adsorption capacity of raw material (AC) increased by pressure of 4000 kPa at 25°C, it is 0.25 wt. % and at -5°C is 0.29 wt. %. Hydrogen adsorption capacity of post treated activated carbon ACP-A at a pressure of 4000 kPa in the temperature of 25°C, is 0.15 wt. % while the temperature of -5°C is 0.18 wt. %. Post treated activated carbon ACP-B gives the hydrogen adsorption capacity at the pressure of 4000 kPa is 0.12 wt. % at 25°C and 0.14 wt. % at -5°C.

Treated activated coal ACP-A has hydrogen adsorption capacity higher than that of ACP-B. The result is interesting since the surface area and pore volume of ACP-A is lower than that of ACP-B. However, up to this stage of examination it is still unclear if the effect of pore diameter has more significant rather than pore volume and/or surface area to

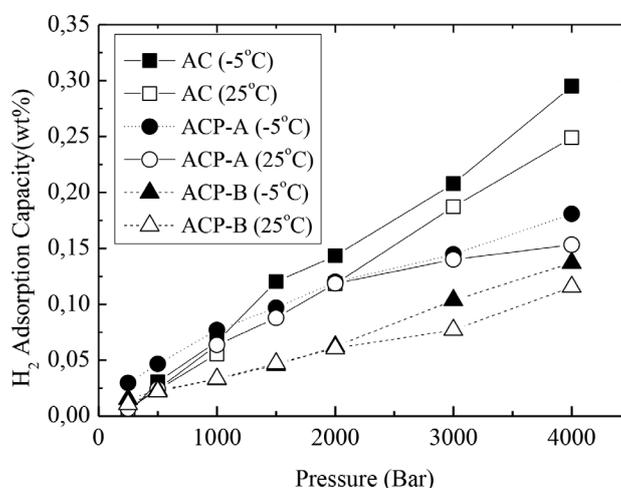


FIGURE 5. Hydrogen adsorption capacity of activated coal (AC) and activated coal with post treatments, dry mechanochemical and pelletized (ACP-A) and wet mechanochemical and pelletized (ACP-B)

the adsorption capacity of hydrogen in adsorbent materials. Even though smaller pores, which also means smaller pore diameter, can adsorb more hydrogen molecules in the low pressure (Thomas 2007).

The interaction between hydrogen molecules with the surface of the adsorbent can be enhanced by the intrinsic electric dipole. Single ionic compounds with hydrogen molecules formed hydrogen clusters showing the electric charge of a substance that plays an important role in generating the interaction of attraction with hydrogen molecules. So that, the activated carbon which has been activated and containing ionic salts such as KCl can increase the hydrogen adsorption capacity due to an increased interaction of hydrogen molecules and materials caused by the electric dipole moment (Sun 2009). However the presence of K_2CO_3 in the materials in ACP-A seem to provide better effect to increase the hydrogen adsorption than KCl alone in ACP-B, though ACP-A has lower surface area than that of ACP-B.

CONCLUSION

Submicrometer coal-based activated carbons were obtained by mechanical milling with PBM. The structure of activated coal become amorphous due to mechanical milling which may cause larger interlayer spacing. The post treatments, i.e. combination mechanochemical process (dry or wet) and pelletization of AC reduce their hydrogen adsorption capacity. It reduces surface area, pore diameter and pore volume of the AC. However characteristics of pelletized of dry mechanochemical process (ACP-A) gives relatively higher hydrogen adsorption capacity than that of wet mechanochemical process (ACP-B).

ACKNOWLEDGEMENTS

Funding support from National Strategic Grant 2011 of Directorate Higher Education, Ministry of National Education Republic of Indonesia is gratefully acknowledged.

REFERENCES

- Ahmadpour, A. & Do, D.D. 1996. The preparation of active carbons from coal by chemical and physical activation. *Carbon* 34(4): 471-479.
- Blackman, J.M., Patrick, J.W. & Snape, C.E. 2006. An accurate volumetric differential pressure method for the determination of hydrogen storage capacity at high pressure in carbon materials. *Carbon* 44: 918-927.
- Fierro, V., Zhao, W., Izquierdo, M.T., Aylon, E. & Celzard, A. 2010. Adsorption and compression contributions to hydrogen storage in activated anthracites. *Int. J. Hydrogen Energy* 35: 9038-9045.
- Harjanto, S., Yunior, S.W., Chodijah, S. & Nasruddin, N. 2013. Hydrogen adsorption behavior of mechanically milled and pelletized coconut shell activated carbon. *Materials Science Forum* 737: 98-104.
- Jiménez, V., Sánchez, P., Díaz, J.A., Valverde, J.L. & Romero, A. 2010. Hydrogen storage capacity on different carbon materials. *Chemical Physics Letters* 485: 152-155.
- Kopac, T. & Toprak, A. 2007. Preparation of activated carbons from Zonguldak region coals by physical and chemical activations for hydrogen sorption. *Int. J. of Hydrogen Storage* 32: 5005-5014.
- Sihite, T. 2012. Low rank coal utilization in Indonesia. *Proc. of International Symposium of Clean Coal Day in Japan*, Tokyo, September 4-5.
- Ströbel, R., Garcke, J., Moseley, P.T., Jörissen, L. & Wolf, G. 2006. Hydrogen storage by carbon materials. *Journal of Power Sources* 159(2): 781-801.
- Sun, X. 2009. Charge induced enhancement of adsorption for hydrogen storage materials. Dissertation, Michigan Technological University, Michigan, USA (unpublished).
- Tellez-Juarez, M.C., Fierro, V., Zhao, W., Fernandez-Huerta, N., Izquierdo, M.T., Reguera, E. & Celzard, A. 2014. Hydrogen storage in activated carbon produced from coals of different ranks: Effect of oxygen content. *Int. J. Hydrogen Energy* 39: 4996-5002.
- Thomas, K.M. 2007. Hydrogen adsorption and storage on porous materials. *Catalysis Today* 120: 389-398.
- Ubago-Perez, R., Carrasco-Marin, F., Fairen-Jimenez, D. & Moreno-Castilla, C. 2006. Granular and monolithic activated carbons from KOH-activation of olive stones. *Microporous and Mesoporous Materials* 92: 64-70.
- Wang, H., Gao, Q. & Hu, J. 2009. High hydrogen storage capacity of porous carbons prepared by using activated carbon. *J. of the Am. Chem. Soc.* 131(20): 7016-7022.
- Yurum, Y., Taralp, A. & Veziroglu, T.N. 2009. Storage of hydrogen in nanostructured carbon materials. *Int. J. Hydrogen Energy* 34: 3784-3798.
- Sri Harjanto*, Latifa N. Noviana, Mia Diniati & Stefano W. Yunior
Department of Metallurgy and Materials Engineering
Universitas Indonesia
Kampus UI, Depok, 16424
Indonesia
- Nasruddin
Department of Mechanical Engineering
Universitas Indonesia
Kampus UI, Depok, 16424
Indonesia

*Corresponding author; email: harjanto@metal.ui.ac.id

Received: 16 April 2014

Accepted: 22 January 2015