INDONESIAN MINING JOURNAL Vol. 17, No. 3, October 2014 : 157 - 165

CARBONIZATION OF BANTEN COAL BY ADDING WATER STEAM; CHANGES ON CARBON FUNCTIONAL GROUPS AND PORE CHARACTERISTICS

KARBONISASI BATUBARA BANTEN DENGAN PENAMBAHAN UAP AIR; PERUBAHAN GUGUS FUNGSI KARBON DAN KARAKTERISTIK PORI

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ABSTRACT

Experimental research and a fundamental study of carbonization of coal have been done by adding steam. The coal sample used in this study was obtained from Bayah, Banten, where the coal was mined by a small-scale underground mining. The study was carried out on a laboratory-scale of adjustable tube furnace reactor. The processes could give carbonized coal with a high calorific value (about 7,600 kcal/kg) and a high fixed carbon content (about 87 wt%). Specific surface area of carbonized products was also interesting as having for 160.5 m2/g. Specific surface area and pore distribution determined by BET techniques and also scanning electron microscope analyses were used to test for the pore and physical properties in the coal. In addition, changes in carbon functional groups and their properties were determined by Fourier Transform Infrared Spectroscopy and Raman Spectroscopy analysis of the products, upgrading process and maturation analyses.

Keywords : carbonization, upgrading process and maturation analyses

SARI

Penelitian dengan percobaan dan studi fundamental tentang karbonisasi batubara telah dilakukan dengan penambahan uap air. Percontoh batubara yang digunakan dalam studi ini diperoleh dari tambang dalam rakyat batubara di daerah Bayah, Banten. Studi ini dilakukan pada percobaan skala laboratorium dengan menggunakan reaktor tabung. Proses ini menghasilkan produk batubara terkarbonisasi dengan nilai kalori yang tinggi sekitar 7.600 kcal/kg dan karbon tertambat yang tinggi sekitar 87 wt.%. Perhitungan luas area permukaan dan distribusi pori produk dilakukan dengan teknik BET dan juga analisis dengan menggunakan scanning electron microscope dilakukan untuk mengetahui karakteristik fisik dari pori produk batubaranya. Selain itu perhitungan dan analisis perubahan gugus fungsi karbon dan karakteristik produk batubaranya dilakukan dengan Fourier Transform Infrared Spectroscopy dan spektroskopi Raman, serta proses peningkatan nilai tambah dan derajat pematangannya.

Kata kunci: karbonisasi, proses peningkatan nilai tambah dan derajat pematangan

Received : 05 February 2014, first revision : 03 June 2014, second revision : 10 October 2014, accepted : October 2014

INTRODUCTION

Low rank coal creates problems during coal utilization. It is generally well-known that total moisture, calorific value (CV) and mineral material in low rank coal inhibit its effective utilization. The increasing requirement to use low rank coal in Indonesia is part of the government's energy development program. The Indonesian coal reserve is approximately 28.9 billion tons, whilst the resource is around 119.4 billion tons (GA-MEMR, 2012). Its quality varies according to the CV and it mostly consists of low (29%), medium (62%), high (8%) and very high (1%). Coal demand grew at the fastest rate of 4.7% per year, followed by oil and natural gas at 2.8%, hydro at 2.6% and renewable energy at 1.3%. The coal demand is mainly driven by electricity generation, as Indonesia promotes the construction of mine mouth coal fired electricity generation plants. Electricity production grew 4.4% annually over 2005 with the total installed generation capacity in 2012 about 33GW is forecasted to grow in 2030 (DGMC-MEMR, 2014). Of this total, coal was accounted for about 42% of the installed capacity requirements. In 2030, coal is expected to account for the largest share of the electricity generation mix at 49%, followed by natural gas (39%), hydro (6%), renewable (3%) and oil (2%) (APERC, 2006). For example, Indonesian coal production reached to 191.25 million tons in 2013, about 75% out of them were exported and about 25% domestically consumed (DGMC-MEMR, 2014). There are four major coal consumers in the country, namely coal power plants, cement industry, manufacturing industry and small scale industry. Power sector (consumption of 34.41 million tons in 2010) and cement and ceramics industry (consumption of 6.31 million tons in 2010) are currently the largest coal consumers and they are estimated to remain so.

One proposed method to convert Indonesian coal was carbonization by adding water steam flows at a high temperature. As water is so common place, it is often regarded as a typical liquid. In reality, water is most typical as a liquid, with its properties at low temperatures are quite different from its properties. When water steam flows and passes through the high temperature of cylindrical columns that is higher than its vapor point, it might change for its physical and chemical properties. Water steam flows molecules will acts as a carrier for volatilized organic compounds. The objective of this study was to investigate about the conversion of coal by carbonization by adding water steam flows at high temperature.

MATERIALS AND EXPERIMENTAL METHODS

Materials

Coal sample was obtained from Bayah, Banten. The coal has an average low of calorific value of 5,730 kcal/kg (air dried basis, adb.). It has high volatile matter and moisture content and relatively high ash content respectively (Table 2). Coal sample was air-dried and ground by jaw crusher and ball mill and rapidly sieved into -40 mesh fraction. X-ray difraction (XRD) was used to study the structural of the coal minerals. Figure 1 shows the XRD pattern for the raw coal. Kaolinite ($Al_2 (Si_2O_5) (OH)_4$), pyrite (FeS_2) and quartz (SiO_2) were detected by XRD in raw coal (Mursito et al., 2011). Table 1 shows XRF analysis results for ash content of raw coal. Aluminum, silica and iron oxides contribute most to the ash. Silica (silicon dioxide, SiO_2) is the main constituent of the ash content of coal. The silica derives from quartz, which relatively occurred in general.

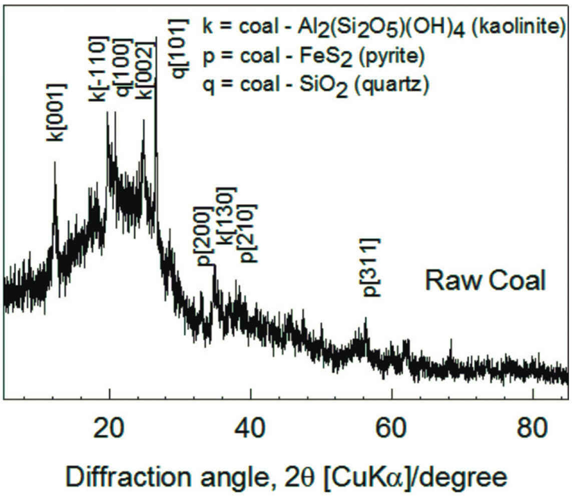


Figure 1. Typical XRD patterns derived from raw coal

Apparatus and Experimental Procedure

The experiments were conducted in a modified adjustable tube furnace reactor (thermolyne) of 60 mm diameter and 320 mm length equipped with automatic temperature control. Steam was produced by a modified double hotplates (ther-

Table 1. Ash analysis of Bayah coal

Ash analysis (wt.%) (d.b)	
SiO_2	48.5
Al_2O_3	42.8
Fe_2O_3	3.9
K_2O	2.6
CaO	1.1
TiO_2	0.7
SO_3	0.3

d.b = dry-basis

molyne) and borosilicate flat bottom glass flasks (pyrex) and capable of producing a maximum steam rate at 400 mL/h in the atmospheric pressure as described in Mursito et al. (2007). Steam was further heated in a heater coil of stainless steel pipe of 45 mm diameter and 400 mm length. 50 g of coal sample was placed inside the middle of tube furnace reactor, inlet and outlet of this tube were sealed with glass-asbestos wool. The inlet of the stainless steel pipe chamber was connected into the steam producer and outlet connected to the flash tank with NaOH 0.1 N solutions. Next, the coal sample was heated in an atmospheric pressure while the reaction temperature was automatically adjusted at 300°C and 600°C at an average heating rate of 6°C/min. The heated steam was flown when the temperature reached to 200 and 500°C. After reaction time of 30, 60 and 120 min, the reactor was rapidly cooled.

Analysis

After cooling, the products were then collected from the reactor and kept in desiccators. The elemental composition of the coal sample was determined prior to acid washing using an elemental analyzer (Yanaco CHN Corder MT-5 and MT-6). Additionally, proximate analysis (based on JIS M 8812), total sulfur analysis (based on JIS M 8819), calorific value analysis (based on JIS M 8814), X-ray fluorescence (XRF) (Shimadzu EX-700) and X-ray diffraction (XRD) (Rigaku Multiflex) were conducted separately. The carbonized coal products were analyzed by Fourier transforms infrared spectroscopy (FTIR) (JASCO 670 Plus) and Raman spectroscopy (JASCO NRS-2000B). The primary components and chemical structure of the raw coal and carbonized coal product were further analyzed by FTIR using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and JASCO IR Mentor Pro 6.5 software for spectral analysis. The measurement parameters for the XRD analysis were as follows: X-ray source Cu Kα; voltage 20 kV; current 20 mA; scanning speed 1°/min; scanning step 0.02°; and scanning

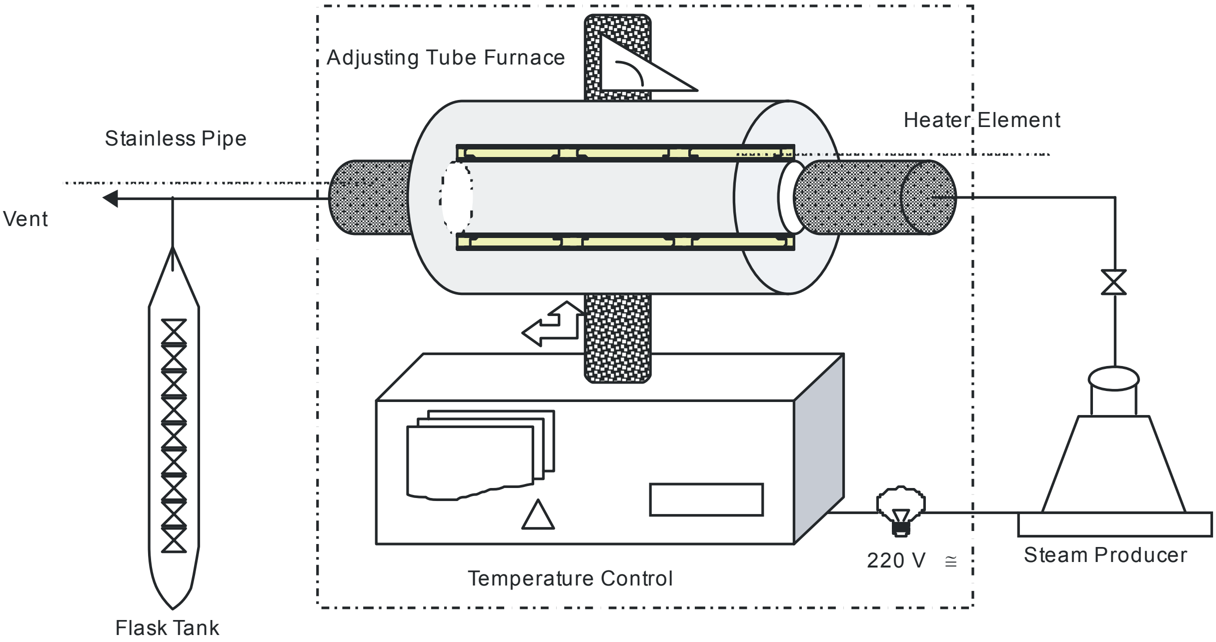


Figure 2. The experimental setup

Table 2. Proximate and ultimate analyses, yield of solid products and calorific value of carbonized coal.

Properties	Raw	Treated temperatures (300°C)			Treated temperatures (600°C)		
		30 min.	60 min.	120 min.	30 min.	60 min.	120 min.
Proximate analysis (wt.%)							
Moisture (a.r)	5.4	3.6	3.0	2.3	2.0	1.9	1.8
Fixed Carbon (d.a.f)	45.50	55.36	55.70	58.89	87.19	86.32	83.70
Volatile Matter (d.a.f)	54.50	44.64	44.30	41.11	12.81	13.68	16.30
Ash (d.b)	17.7	16.2	17.3	18.4	26.8	25.0	23.9
Ultimate analysis (wt.%) (d.a.f)							
C	71.03	72.42	73.26	74.50	84.02	85.37	86.16
H	5.63	5.47	5.45	5.31	3.88	2.76	2.69
N	1.57	1.60	1.63	1.65	1.91	1.91	1.84
O (diff.)	18.64	17.48	16.66	15.25	7.87	7.65	6.35
S	3.12	3.03	2.99	3.30	3.28	2.31	2.96
Yield of solid products (w.t%) (d.b)	-	92.63	92.44	89.12	66.72	64.34	63.82
Calorific value (kcal.kg-1) (d.a.f)	7,359	7,378	7,43	7,476	7,632	7,605	7,478

d.b = dry basis; a.r = as received basis; d.a.f = dry ash free basis; diff. = differences

range (2θ) 5 to 85. The pore size distribution, BET surface area (SBET), micro pore, and external surface area of the raw coal and carbonized coal were obtained from the N_2 adsorption isotherms at 77 K determined in a semiautomatic Autosorb-1 analyzer (Quanta chrome).

RESULTS AND DISCUSSION

Carbonized Coal Properties

In the carbonization process, there are some variables that may be controlled, allowing optimization of some parameters such as yield and the physical and structural characteristics of the products. In this study, five variables of the activation process were considered: carbonization temperature, heating rate, steam flow and residence times. The coal was not treated before its use. Lower steam flow reduces the formation of the char pores, while higher flows may drop the temperature in the reactor and produce very humid activated carbon products. In general, the choice of the residence times for the activation depends on the desired porous structure distributions and yield.

Table 2 shows that carbonized coal yield was much affected by the differences of temperature at 300 and 600°C. The total yield was decreased by increasing the residence times and temperature. Percentage loss of yield is always performed due to the decreasing of moisture content and volatile matter. At 300°C and 120 min, total yield of carbonized coal have maximum limit of products on 89.12%. Percentage loss of yield was performed when increasing temperature at 600°C and 120 min. It has maximum yield of coal products on 63.82%.

Carbonized coal produced very remarkably high calorific value compared with raw coal sample for every treatment conditions on moisture and ash free basis (dry ash free, daf). Calorific value increased with increase in the residence time when the temperature was 300°C, it reached a maximum calorific value of 7476 kcal/kg at 120 min. At 600°C, it reached a maximum calorific value of 7632 kcal/kg for a residence time of 30 min, but it decreased when the residence time was increased to 120 min.

Proximate analysis was also conducted for fixed carbon content and volatile matter development of carbonized coal. Fixed carbon content increased for a maximum of 41% and volatile matter decreased for a minimum of 58.89 wt% with increase of residence times to 120 min and temperature treatment especially at 300°C. At 600°C, those reached a maximum fixed carbon of 87.19 wt% and for a minimum volatile matter of 12.81 wt% for a residence time of 30 min., but it decreased when the residence time reached to 60 and 120 min.

FTIR structural analyses during carbonization

The process occurring during the carbonization of coal can be investigated either by studying of the behavior development of raw coal sample under increasing of temperature and residence times or the carbonized coal itself. Figure 3 shows FTIR spectra results for the raw coal and carbonized coal at different treated temperature and residence times. Determination of the peaks in each spectrum of the main functional groups was obtained using JASCO IR Mentor Pro 6.5 software and reference to several publications (Painter et al., 1981; Ibarra et al., 1996). In this works, JASCO FT/IR-670Plus spectrometer has been applied to the characterization and qualitatively determined the development of chemical structures and organic compounds of coal. Other peaks in each spectrum obtained for minerals and related inorganic compounds have been determined in other published studies (Farmer 1974; Velde and Martinez, 1981). The strong bands in the 3,620 and 3,690 cm-1 regions are due to the Si–OH stretching modes of silicate clay minerals (kaolinite), which are confirmed by XRD analysis. The clay was also identified in the OH stretching absorption 3,700-3,400 cm^{-1} region, and in particular the band at 3,620 cm^{-1}, distinguishes kaolinite in the raw coal and carbonized coal spectra. The bands observed in the FTIR spectrum of the raw coal were in agreement with the minerals identified by XRD.

Organic OH stretches occur around 3,380 cm^{-1}, while aliphatic CH_2 and CH_3 stretching vibrations can be recognized at 2,930 and 2,860 cm^{-1}, respectively. In addition, significant changes in the oxygen content of the functional groups can also be observed in the 1,800-1,100 cm^{-1} zone. Increasing of temperature to 600°C has dramatically changed the chemical behavior of coal. Many OH bonds, aliphatic chains and some aromatic nucleus were disappeared at 600°C. The relative intensities of the C=O highly conjugated at 1,620 cm^{-1} were observed under all conditions. Aromatic ring stretching vibrations are also observed at 1460 cm^{-1} and decreased in relative intensity at 600°C. C–O–R structures of ethers were observed at 1270 cm^{-1}, vanishing at all treated temperature of 600°C due to decomposition by oxidation. Aromatic C–H out-of-plane bending mode vibrations were observed at lower wave numbers (900–700 cm^{-1}).

Raman spectroscopy structural analyses during carbonization

Raman spectroscopy should be ideal for independently assessing coal maturity and offers a number of advantages (Quirico et al., 2005). It is also nondestructive and requires very small amounts of material. In the first-order region, the graphite band (G band) was originally estimated around 1575 cm^{-1} by Tuinstra & Koenig (1970). The band occurring at 1,350 cm^{-1} (D1 band) is intense and very wide in poorly ordered carbons. The 1620 cm-1 band (D2 band) appears as a shoulder on the G band. The 1,500 cm^{-1} band (D3 band) is present in poorly ordered carbons as a very wide band (Beyssac et al., 2002). Band assignments of coal samples related coal rank and coal char are also presented by Ulyanova et al. (2014) and also Li et al. (2006).

The spectra exhibit spectral variations correlated with the increase of the maturation grade (Quirico et al., 2005) and also coal rank and quality. All Raman spectra of upgraded coal samples have similar shape. Increasing the maturity leads to the narrowing of both bands, the decrease of the inter-band intensity and the appearance of substructures in the D-band (Quirico et al., 2005). The spectral shape of the G-band and D-bands are sensitive to maturity. The width of the G- and D-bands continues to decrease, but the relative intensity of the D-band increases.

Figure 4 shows the Raman spectra of selected carbonized coal at 300 and 600°C for 30 to 120 min. Relative area intensity of G band for all carbonized coal was increased and narrower than the raw coal. No correlation between the quality of carbonized coal and the positions of Raman shift of raw coal and the relative intensity was found. The developments of G band were interesting as indicated that the maturity of carbonized coal increased. However, one can observe that in all samples were projected to amorphous carbon structure and present as poorly ordered carbons because D-band was intense and occurred. The all 600°C Raman spectrums shapes has slightly similar for anthracite coal spectra at previously published by other researchers (Van Doorn et al., 1990).

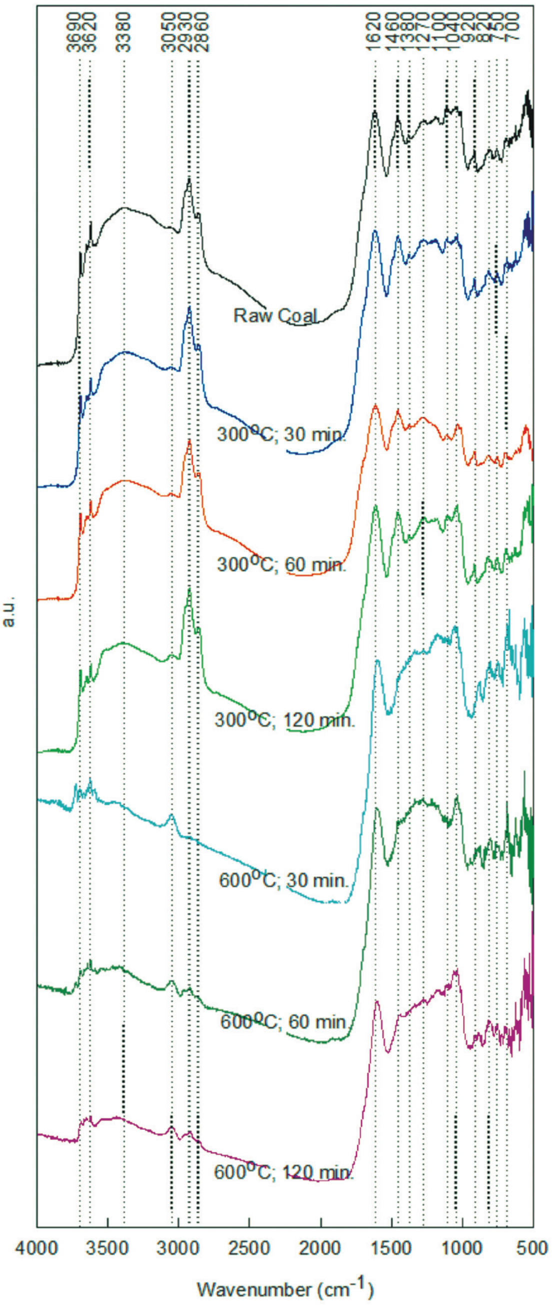


Figure 3. FT/IR spectra of selected raw coal and carbonized coal at different treated temperature

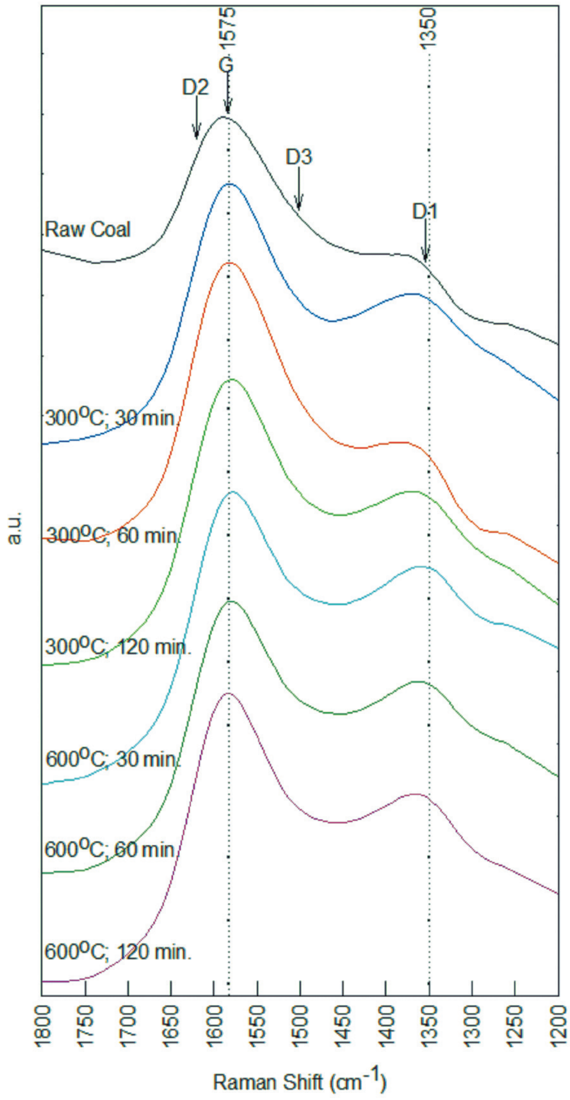


Figure 4. Raman spectra of selected raw coal and carbonized coal at different treated temperature

BET, pore development and SEM examination and analyses during carbonization

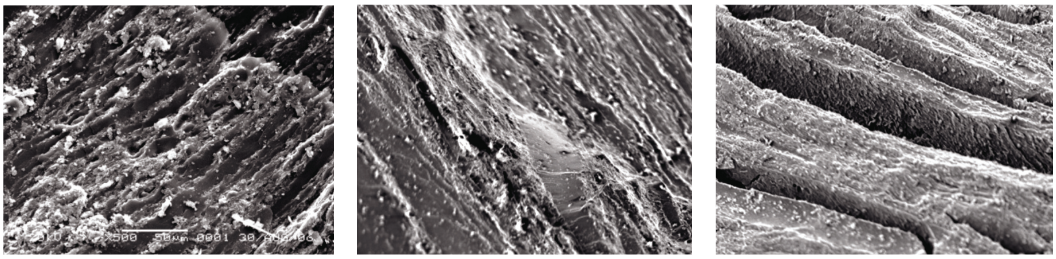
The pore size distribution, BET surface area (SBET), micropore, and external surface area of the raw coal and carbonized coal were obtained from the N_2 adsorption isotherms at 77 K determined in a semiautomatic Autosorb-1 analyzer (Quantachrome). However, the total specific surface area (STA), the internal specific surface area (STI), and the external specific surface area (SEXT) calculated by the t-plot method are used when it is necessary to divide the specific surface area into individual parts corresponding to the micropores, the mesopores, and the macropores. Here, SEXT corresponds to the mesopores and macropores, and STI corresponds to the micropores (Shimada et al., 2004). The SBET, STA, STI, and SEXT values and the ratio of the internal to the external specific surface area (STI/SEXT) for the raw coal and carbonized coal are listed in Table 3.

Table 3. Specific surface area by the BET method and the t-plot method of the raw coal and carbonized coal at different treated temperature

Samples	SBET	STA	STI	SEXT	STI/SEXT
	(m2/g)	(m2/g)	(m2/g)	(m2/g)	
Raw Coal	3.288	3.288	0	3.288	0
B 300°C-30 min.	2.426	2.426	0.696	1.730	0.402
B 300°C-60 min.	5.460	5.460	0	5.460	0
B 300°C -120 min.	4.685	4.685	0	4.685	0
B 600°C -30 min.	160.500	160.450	59.050	101.400	0.582
B 600°C -60 min.	121.700	121.710	51.860	69.850	0.742
B 600°C -120 min.	109.200	109.210	43.230	65.980	0.626

Regarding the SBET of the carbonized coal treated 600°C in present of steam; the SBET of the carbonized coal has a higher value than that of the raw coal and carbonized coal treated at 300°C for all residence time condition. SBET decreased with an increase in the residence times. At 600°C, it reached a maximum value of 160.5 m^2/g at 30 min, then SBET decreased when the residence time was increase to 60 and 120 min.

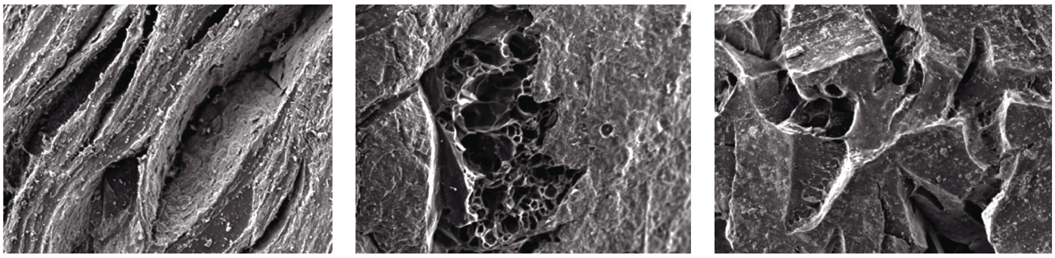
Furthermore, (STI/SEXT) of the carbonized coal at 600°C has reached a lower value than 1. Therefore, it is believed that the mesopores and macropores were well-developed when compared with the micropores. If the condition reached a high value of 1 or more, reason for this is that the development of the mesopores and macropores is small as compared with that of the micropores. Activation by means of presence of steam in the system eliminates the disorganised carbon, exposing the aromatic sheets to the action of activation agents and leads to development of a microporous structure (Manocha, 2003). Also, SEM photograph of upgraded coal shows macro-structures related to the destroying of coal matrixes and pores and cracked structures of coal matrices (Figure 5).



Raw coal

Carbonized coal at 300°C for 120 min

Carbonized coal at 600°C for 120 min.



Carbonized coal at 600°C for 30 min.

Carbonized coal at 600°C for 60 min.

Carbonized coal at 600°C for 60 min.

Figure 5. SEM photograph of Bayah coal and carbonized coal

CONCLUSION

The Bayah coal has been treated by carbonization in order to produce activated carbon precursor and/or fuel products. Carbonized coal yield as a product of coal char was much affected by the differences of the treated temperature of 300 and 600°C. The total mass yield was decreased by increasing the residence times and temperature. FT/IR spectra of carbonized coal were also affected by increasing of temperature and residence times. Raw and carbonized coals at 300oC have almost the same interpretations of FT/IR spectra. Increasing of temperature to 600oC has dramatically changed the organic properties of coal such as OH bonds, aliphatic chains and some aromatic nucleus. Carbonized coal using water steam flows in the thermal environment has physically similarities for activated carbon pores structures. By these physical properties of upgraded coal, the possibility of its utilization is not only for activated carbon purposes but may also used for fuel energy.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the contributions and assistance of the Laboratory of Mineral Engineering and Chemistry; and Research Group of Coal and Energy, Lestari Simanjuntak and Restiana Dewi, University of Pendidikan Indonesia (UPI) for assisting the authors during the fieldwork and laboratory work.

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