OBTAINING OF HIGH DENSITY CARBON MATERIALS BY COKE SINTERING RESULTING FROM HEAT TREATMENT OF TAR FOR APPLICATIONS IN SENSORS MANUFACTURE

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In this research, high-density and high-strength carbonized carbon blocks were manufactured by coke sintering resulted from heat treatments of biomass pyrolysis tar. First, the molecular weight distribution of the tar was controlled through a pressurized heat treatment at 365°C and then this heat-treated tar was treated using a delayed coking system to obtain the self-sintering coke. Finally, carbon blocks were molded from the self-sintering coke and carbonized at 1100°C for 2h. Through rapid decomposition of the high molecular weight compounds in the tar at 360°C, the molecular weight distribution of tar was confirmed to be controllable by this treatment stage. During carbonization was observed a swelling in carbon blocks manufactured that contain more than 15 wt% of volatile matter from 150-500°C. The optimum conditions of the two heat treatments stage were established to be 310°C for 3 h and 500°C for 1.5 h. The highest density and highest strength of the carbonized carbon blocks manufactured were 1.44 g/cm³ and 68.7 MPa, respectively.

Keywords: high density carbon; biomass tar; heat treatment; coke sintering.

INTRODUCTION

Various kinds of carbon materials such as blocks, powders, emulsions are widely used as important components in the modern industry. For example, carbon materials are employed as biomedical substances, materials used in chemical sensors manufacture for applications in optoelectronics or in medical devices, electronic stuff, aerospace items, and so on (Delpont and Badenhorst, 2016; Xiao *et al.*, 2016). In the early stage of the carbon industry, tar, pitch, naphtha and coke were developed as raw materials for the manufacture of graphite powder (Choi *et al.*, 2017; Mearz *et al.*, 2018). With the accelerated development of carbon industries, the manufacturing and processing techniques for artificial graphite blocks have been developed precisely and efficiently (Xiao *et al.*, 2016; Lee, Kang and Roh, 2015).

The processes for the graphite manufacturing include the following steps: (i) The process of coking to eliminate the volatile matter, (ii) The grinding and sieving steps for particle sizing, (iii) The mixing of coke with the binder to prevent the phenomenon of swelling, (iv) Block formation of different forms and dimensions, following of calcination, (v) Repeating the steps of impregnation, drying and calcination to obtain a high density material with high strength, and (vi) Graphitization of the resulted material from before step (Du *et al.*, 2010; Chen *et al.*, 2012; Shen *et al.*, 2015). In this processes the important factors are the coke types and the mixing ratio of coke and binder, but at the same time, to obtain high density blocks of graphite, the steps of impregnation, drying and calcination need to be repeated, and this represents a critical problem because to repeat the impregnation and calcination processes can increase the manufacturing costs and time. In order to eliminate these deficiencies, many studies were achieved to investigate other advanced methods, such as using of mesophase

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powder (Li *et al.*, 2011; Zhao *et al.*, 2013; Cheng *et al.*, 2015), mesoporous carbon microbeads (MCMB) (Fang *et al.*, 2015; Shen *et al.*, 2011), self-sintering coke (Kocafe *et al.*, 2016), or adding a sintering agent (Shen *et al.*, 2013).

In this research, high density and high strength carbonized carbon blocks were obtained by coke sintering resulted from heat treatments of biomass pyrolysis tar. First, the molecular weight distribution of the tar was controlled through a pressurized heat treatment at 365°C and then this heat-treated tar was treated using a delayed coking system to obtain the self-sintering coke. Finally, carbon blocks were molded from the self-sintering coke and carbonized at 1100°C for 2h.

EXPERIMENTAL PART

Material and Methods

For obtaining of high density carbon block, it was used as raw material the biomass tar, resulted from residual biomass pyrolysis, so it is described in our previous research (David, 2013). The biomass tar was mixed with tetrahydrofuran (99.9% from Sigma-Aldrich) in a 1:1 ratio, and then the mixture was refined by a pressure filtering process. Then, the biomass tar was separated of tetrahydrofuran in a rotary evaporator, by increasing the temperature from room temperature to 75°C. Table 1 contains the elemental analysis, insolubility and ash content of the refined biomass tar.

Table 1. The elemental analysis, insolubility and ash content of the refined biomass tar

Ultimate analysis (wt.%)					Proximate analysis (%)		
C	H	N	S	O	TI	QI	Ash
91,75	5,18	1,71	0,67	0,09	5,78	-	0,10

a-by difference; TI-Toluene Insolubility; QI-Quinoline Insolubility

The scheme of manufacture method to obtain the carbonized carbon block by heat treatments is presented in Figure 1.

Figure 1. The scheme of heat treatments in two steps for manufacture the carbon block from biomass tar

The refined biomass tar was first heated at temperatures of 310, 330 and 365°C for 1 and 3 h in the pressurized system (the pressure was increased to about 6, 9, 12, and 15 bar, depending on the temperature, respectively). Second, the resulted heat treated tar from stage I (C_{ST-I}) was once again heated to 500°C in the coking system (2nd stage treatment) to produce coke (C_{ST-II}). The resulted coke from stage II was grinded, sieved to under 75 mm in size, and then extruded into small plates with the dimensions of 12x12x3 mm and 30x15x3 mm using a cold high pressure press (280 bar). These rectangular plates were each prepared three times according to the manufacture conditions and finally, the raw carbon blocks were carbonized at 1100°C for 1 h to 3 h at the heating rate of 2°C/min. As obtained carbonized carbon blocks were analyzed to establish hardness, bending strength and surface texture.

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Analytical Tools Used

The proximate and ultimate analysis of the refined biomass tar, C_{ST-I} and C_{ST-II} samples was made using a FLASH-2000 Elemental Analyzer. The insolubility was determined based on ASTM D-2318 and ASTM D-4072, by quinolone insolubility (QI) and toluene insolubility, respectively. Thermogravimetric analysis was performed using TGA, STA 409 PC, Netzsch, Germany, analyzer and the weight loss was examined at a rate of 10°C/min at 900°C under a N₂ flow of 15 ml/min. The image of the carbon block surface was obtained by scanning electron microscopy (SEM, using Jeol JSM-7000, JEOL Ltd., Japan). The flexural strengths of carbon blocks were determined using a universal testing machine (WL2100, WITHLAB, Korea) based on the ASTM C-1161.

RESULTS AND DISCUSSION

The content of carbon, hydrogen, nitrogen and sulfur into C_{ST-I} samples prepared under various temperature conditions and times are presented in Table 2.

Table 2. Elemental analysis of C_{ST-I} samples prepared under various heating temperatures and different times

Conditions for Stage I	C(wt.%)	H(wt.%)	N(wt.%)	S(wt.%)	C/H ratio
310°C; 1 h	90.83	5.64	0.62	0.31	1.34
330°C; 1 h	91.78	5.68	0.75	0.35	1.35
365°C; 1 h	91.96	5.58	0.87	0.41	1.37
310°C; 2 h	91.53	5.54	0.71	0.38	1.38
330°C; 2 h	91.65	5.49	0.79	0.46	1.39
365°C; 2 h	91.79	5.42	0.83	0.47	1.41
310°C; 3 h	92.73	5.43	0.74	0.49	1.42
330°C; 3 h	92.89	5.33	0.81	0.53	1.45
365°C; 3 h	93.04	5.61	0.93	0.54	1.38

With the increasing of reaction temperature and reaction time, the C/H ratio increased. The C/H ratio for sample treated at 310°C for 3h was higher than that samples treated at 310°C for 2h and 1h, respectively. On the other hand, the C/H ratio of sample treated at 330°C for 3h was higher than that of samples treated at 310°C for 2h and 1h respectively. These results suggest that the compounds with low molecular weights were decomposed or polymerized into polycyclic aromatic hydrocarbons (PAHs), having higher molecular weight. However, so can be seen in table 2, the C/H ratio of the sample treated at 330°C for 3 h was higher than that of the sample treated at 365°C for the same time (3 h) and this results indicate that the aromatic bond was fast broken at the temperature of 365°C for 3 h under a pressure around 15 bar (Im *et al.*, 2017). Additionally, it can be demonstrated that the distribution of the molecular weights of the compounds in the refined biomass tar can be controlled by the 1st step of treatment. The stage II of treatment was performed at temperature of 500°C for 1 to 3h.

Analytical Tools Used Morphological and Mechanical Characteristics of Sintered Carbon Blocks

The weight loss was measured by the thermogravimetric analyses of the C_{ST-II} samples. A phenomenon of swelling was observed for the carbon blocks manufactured at 330°C and 365°C for 1h, they contained over 15 wt% volatile matter. It was observed that the carbon blocks with less than 15 wt% volatile matter kept their rectangular form after carbonization. The samples treated in first stage at 310°C; 330°C; 365°C for 3 h

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and which were treated for 1.5 h in the stage II, exhibited a weight loss of less than 15wt.% and shrinkage of volume less than 20 wt%.

Table 3 present that optimal conditions for the 2nd step of treatment to obtain the high density carbon block and this are 500°C for 1.5 h. Thus, C_{310-3-1.5} has exhibited an apparent density of 1.44 g/cm³, which was higher than the reported density of approximately 1.40 g/cm³ (Zhou and McGinn, 2006). Also, C_{310-3-1.5} showed the best mechanical properties having a flexural strength of 68.7 MPa.

Table 3. Characteristics of the carbon blocks resulted after the second stage of treatment (temperature treatment for stage II of treatment 500°C)

Sample *C _{x-y-z}	Total loss	Weight loss ratio (wt.%)			Vol.shrinkage Flex.stength (%)	Density (g/cm ³) (MPa)	
		150-500°C	500-650°C	650-1100°C			
C _{310-1-1.5}	23.54	11.52	2.26	9.87	35.68	1.35	28.3
C _{330-1-1.5}	18.21	7.18	2.05	8.72	25.27	1.22	4.7
C _{365-1-1.5}	20.68	15.25	2.26	2.85	21.28	1.14	2.8
C _{310-3-1.5}	24.36	11.56	2.83	9.74	40.32	1.44	68.7
C _{330-1-1.5}	23.52	10.68	3.01	9.61	33.58	1.33	28.3
C _{365-1-1.5}	-	18.22	2.46	-	-	-	-
C ₃₃₀₋₃₋₃	14.24	6.14	1.77	6.44	29.75	1.32	29.2

*C_{x-y-z} denotes: x-temperature value in the first stage of treatment; y-time of treatment in the first stage; z- time of treatment in second stage.

The cracks containing the size around 100-500 µm were found in C₃₆₅₋₃₋₁, as is shown in Figure 2a. C_{310-1-1.5} presented swelling phenomena, as showed in Figure 2b. For C_{365-3-1.5} carbonized sample, the rectangular plate of the original shape disappeared completely.

Figure 2. The change appeared in carbon block after carbonization: (a)-SEM image for C_{365-1-1.5}; (b)-SEM image for C_{310-1-1.5}; (c) - SEM image for C_{365-3-1.5}

The SEM images of surfaces for carbon blocks carbonized at 1100°C are presented in Figure 3. In Figure 3(a, c and d), the particle forms are quite difficult to notice. In Figure 3(b, e and f), can be observed small cracks between different particles. Also, an important quantity of particle cracks between 100 and 500 mm can be observed in Figures 2(a) and 3(c).

The results for the weight loss in the carbonization process showed that the samples range of treatment temperatures can be divided into three ranges, by dividing the treatment temperatures. C_{310-1-1.5} and C_{310-3-1.5} had a significant difference in the amount of weight loss in the range temperature of 500°C - 650°C, and C_{310-3-1.5} and C_{330-3-1.5} differ in their weight losses in the temperature range of 150°C - 500°C. The amount of weight loss from 150°C to 650°C showed to be a main factor that affects the mechanical bending strength. The small cracks between coke particles, reduce mechanical properties, and were more pronounced for the samples when the volatile matter at 500-650°C were smaller, as it can be seen in Figure 3.

Figure 3. SEM images of carbon blocks carbonized at 1100°C: (a)-C_{310-1-1.5}; (b)-C_{330-1-1.5}; (c)-C_{365-1-1.5}; (d)-C_{310-3-1.5}; (e)-C_{330-3-1.5}; and (f)-C₃₃₀₋₃₋₃;

However, comparing the results for C_{330-1-1.5} and C₃₃₀₋₃₋₃ in Table 2, the flexural strength of C₃₃₀₋₃₋₃ is better. This result maybe is due to the occurrence of small cracks that could reduce the flexural strength for carbon blocks when the volatile matter is evaporated in the temperature range of 650-1100°C and the degree of volume shrinkage decreased, these results being in agreement with other studies (Cheng *et al.*, 2015; Cheng *et al.*, 2013).

Figure 4 shows the optimum conditions for the first stage of treatment to manufacture high density carbon blocks based on the weight losses and volume shrinkages of C_{310-1-1.5}, C_{330-1-1.5} and C_{365-1-1.5} samples.

Also, it can be observed that a decrease in the the volume shrinkage took place when the reaction temperature for the first stage treatment has increased. In addition, the weight loss ratio of the C_{365-1-1.5} sample was greater than that of C_{330-1-1.5}, and this is due to the decomposition of high molecular weight compounds at a reaction temperature above 330 °C. According to this analysis, it can be concluded that the amount of high molecular weight produced in the stage I of treatment lead to decreasing of the volume shrinkage, the density and the mechanical properties.

Figure 4. Effect of the heat treatment temperature on volume shrinkage and weight loss during first stage of treatment (C_{310-1-1.5}, C_{330-1-1.5} and C_{365-1-1.5} samples)

CONCLUSIONS

The high density carbon blocks were developed by coke sintering of the biomass tar. As the reaction temperature increased during the first stage of treatment, the C/H ratio increased. The low molecular weight compounds of the C_{ST-Is} increased if the reaction temperature was above 330°C. All of the sintering coke obtained by the two stage of heat treatment starting from biomass tar present a uniform mesophase structure. The carbon blocks containing over 15 wt% volatile matter at 150-500°C, were swollen. In addition, the small cracks in the carbonized carbon blocks containing less than 2 wt%

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volatile matter at 500-650°C were observed. The weight loss, from 150 to 650°C during carbonization process, was due to active volume shrinkage, resulting sample with a high density. The amount of weight loss from 650-1100°C during the carbonization process was found to be a key factor that reduced the mechanical properties. Thus, the optimum conditions of the first stage and the second stage of heat treatment were confirmed to be 310°C for 3 h and 500°C for 1.5 h, respectively.

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