

## **THERMAL AND STRUCTURAL PARAMETERS ANALYSIS OF CARBON PELLETS PREPARED FROM KOH TREATED PRE-CARBONIZED COTTON CELLULOSE**

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### **ABSTRACT**

Carbon pellets (CPs) precursor (cotton cellulose) was first pre-carbonized at low carbonization temperature, milled for 20 h and sieved to produce self-adhesive carbon grains (SACG). The SACG was treated with KOH having concentration from 0 to 0.07 Moles ( $M$ ) and converted into green pellets (GPs) by applying 12 metric tones compression load on 2 g of samples in a mould with diameter of 2.72 cm. These GPs were carbonized up to the temperature of 500 °C-1000 °C, using a multi-steps heating profile. The CPs produced was washed by distilled water until reaching a pH of 6. The thermogravimetric data showed that with increasing KOH concentration, the weight loss of the samples at 600 °C markedly decreased, particularly at 0.07  $M$  KOH concentration, and the maximum rate of weight loss for all the treated samples was higher and occurred at lower temperatures. The interlayer spacing ( $d_{002}$ ), stack height ( $L_c$ ) and stack diameter ( $L_a$ ) of the turbostratic crystallites in the CPs estimated from X-ray diffraction data showed that (a) for the CPs from the untreated GPs,  $d_{002}$  increased with increasing carbonization temperature and linearly increased with  $1/L_a$ , (b) for the CPs (1000 °C) from the treated GPs,  $d_{002}$  decreased with increasing KOH concentration but linearly increased with  $1/L_a$ . These findings indicate that the CPs have larger dimension of the turbostratic crystallites at higher temperatures, and such a dimension decreased for the GPs treated with higher KOH concentration.

### **INTRODUCTION**

Thermal behavior of a carbon precursor has been widely studied using the thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA). It deals with the measurement and analysis of the weight change of a sample due to thermal decomposition during carbonization process, as a function of temperature and time of heating carried out in a controlled environment. The thermal decomposition of cellulose of different molecular weights is dependent on its molecular weight [1]. It was observed that carbonization behavior of KOH treated coal was different than that of the untreated coal [2]. The KOH treatment on carbon precursors was found effective in enhancing the pore development in the sample during the carbonization of precursors such as oil palm stone[3] and pre-carbonized oil palm empty fruit bunches[4]. In our

present study, the thermal behavior of the pre-carbonized cotton cellulose treated with different concentration of KOH was investigated using TGA and DTGA.

Analysis of certain carbon structure can be made in terms of the dimension (stacks height ( $L_c$ ) and width ( $L_a$ )) of the graphite-like crystallites that are randomly distributed and oriented through out the samples. Each crystallite consists of a number of near-parallel carbon layers that form the stacks height and width, and the nearest layers are separated by an interlayer spacing  $d_{002}$ . Both  $L_c$  and  $L_a$  were found to change simultaneously during carbonisation [5], and  $L_c$  was observed to be dependent on the crystallinity of the precursor [6]. The alkaline treatment of the cellulose that can change the cellulose crystallinity is therefore expected to affect the crystallites dimension resulted after carbonization [7]. In the present work, cotton cellulose will be used as carbon precursor, where the carbonization process was carried out in nitrogen gas up to 500 °C to 1000 °C in order to produce carbon pellets from the powder of the untreated and KOH treated precarbonized cotton (SACG). The aim of this work is to carry out the thermogravimetry analysis on the untreated and treated SACG, and also to study the structure of carbon pellets prepared from these SACG in terms of the interlayer spacing ( $d_{002}$ ), stack height ( $L_c$ ) and stack diameter ( $L_a$ ) of the turbostratic crystallites in the carbon pellets using X-ray diffraction technique.

## MATERIALS AND METHODS

The cotton-ball samples were pre-carbonized up to 300 °C in a heating chamber in vacuum environment for 4 h, milled for 20 h and sieved to produce self-adhesive carbon grains (SACG) that can pass through a 53 microns sieve. The SACG powder produced were treated for 16 h with KOH having concentration from 0 to 0.07 moles ( $M$ ), and then dried in oven at 100 °C and converted into a green pellets (GPs) by applying 12 metric tones compressive pressure on 2 g of powder. These GPs were carbonized from 500 °C to 1000 °C in nitrogen environment using multi-steps heating profiles (Vulcan Box Furnace 3-1750) programmed as 1 °C per minute from room temperature to 375 °C: remains 1 h at 375 °C, 3 °C per minute from 375 °C to 800 °C and 5 °C per minute from 800 °C to 1000 °C, and remains 5 minutes at 1000 °C [8]. The carbon produced were washed thoroughly by hot distilled water to remove impurities until a pH of 6, and dried in an oven at 100 °C for 4 h.

### *Thermogravimetric Analysis and Differential Thermogravimetric Analysis*

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA) were carried out on the raw cotton cellulose, untreated and treated SACG powders with KOH of 0 to 0.07  $M$  using the Rigaku Thermo Plus TG8120 instrument from 20 °C – 600 °C at a heating rate of 10 °C/min under a flow of nitrogen gas. The data were collected in terms of the weight loss and rate of weight loss against the temperature.

### *X-ray Diffraction*

The samples for the X-ray diffraction were the carbon pellets prepared from the

carbonization of the untreated green bodies from 500 °C to 1000 °C, and also the carbon pellets prepared from the carbonization of the green pellets from the KOH treated (0.0 to 0.07 M) SACG. The diffraction intensity of the carbon pellets was measured using an X-ray diffractometer (Bruker Advanced Solution AXS D8) operating at 40 KV and 30 mA, with Cu K<sub>α</sub> X-ray of wavelength ( $\lambda$ ) 1.5404 Å. The measurements were carried out over a range of the diffraction angle,  $2\theta$ , from 2.3° – 60° in step size of 0.04°.

The crystallite parameters such as stack height ( $L_c$ ), and stack diameter ( $L_a$ ) of the graphite-like crystallites can be calculated from the diffraction intensity using the Scherer's equation and Warren's correction for instrumental line broadening [9]

$$L_{c,a} = \frac{K\lambda}{\beta_{c,a} \cos\theta} \quad (1)$$

where  $\beta_{c,a}$  is the width at half-height of symmetrical shape of the diffraction peaks,  $\theta$  is angular position of the diffraction peak,  $\lambda$  is the wavelength of X-ray diffraction,  $K$  is a shape factor which is equal to 0.9 for  $L_c$  and 1.84 for  $L_a$ . In the case of carbon samples,  $L_c$  and  $L_a$  correspond to the (002) and (100) diffraction peaks respectively.

## RESULTS AND DISCUSSIONS

Typical TGA curves of the samples presented in Figure 1 (a) clearly shows that the KOH treatment influences the carbonization behavior of the samples, where above 350 °C, increase in KOH concentration significantly reduces the weight loss or increase the yield of the samples, particularly for the treatment at 0.07 M, as can be seen in the plot of weight loss at 600 °C against the KOH concentration (Figure 2 (a)). This higher yield is due to the presence of compounds resulted from the KOH reaction in the samples during carbonization [2,3]. Figure 1 (a) also shows a clear difference of weight loss behavior between the raw cotton ball (cellulose) and the pre-carbonized cotton ball, for example at 600 °C, their yields are 15% and 30% respectively. This is an expected difference because the latter sample has already lost some of its weight during pre-carbonization process. However, the overall shapes of their TGA curves are almost similar; indicating that the SACG still retains the cellulosic structure of the cellulose.

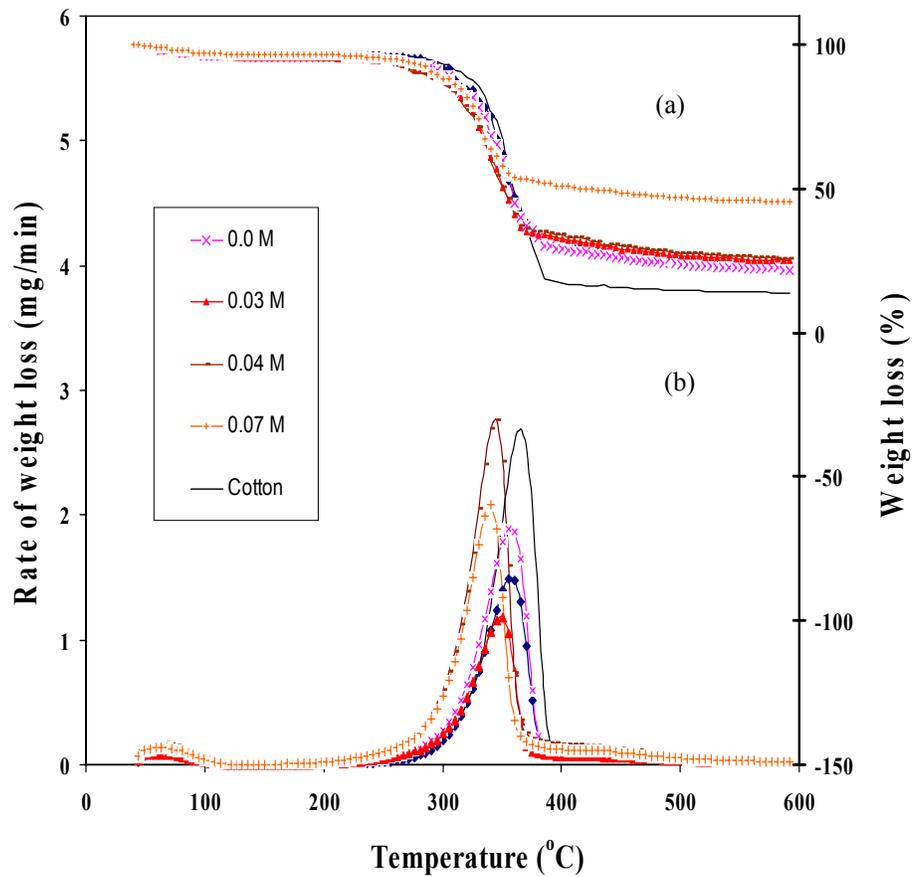


Figure 1: TGA and DTGA of cotton cellulose, SACG, and SACG treated with KOH from 0 M to 0.07 M, heat treated up to 600 °C

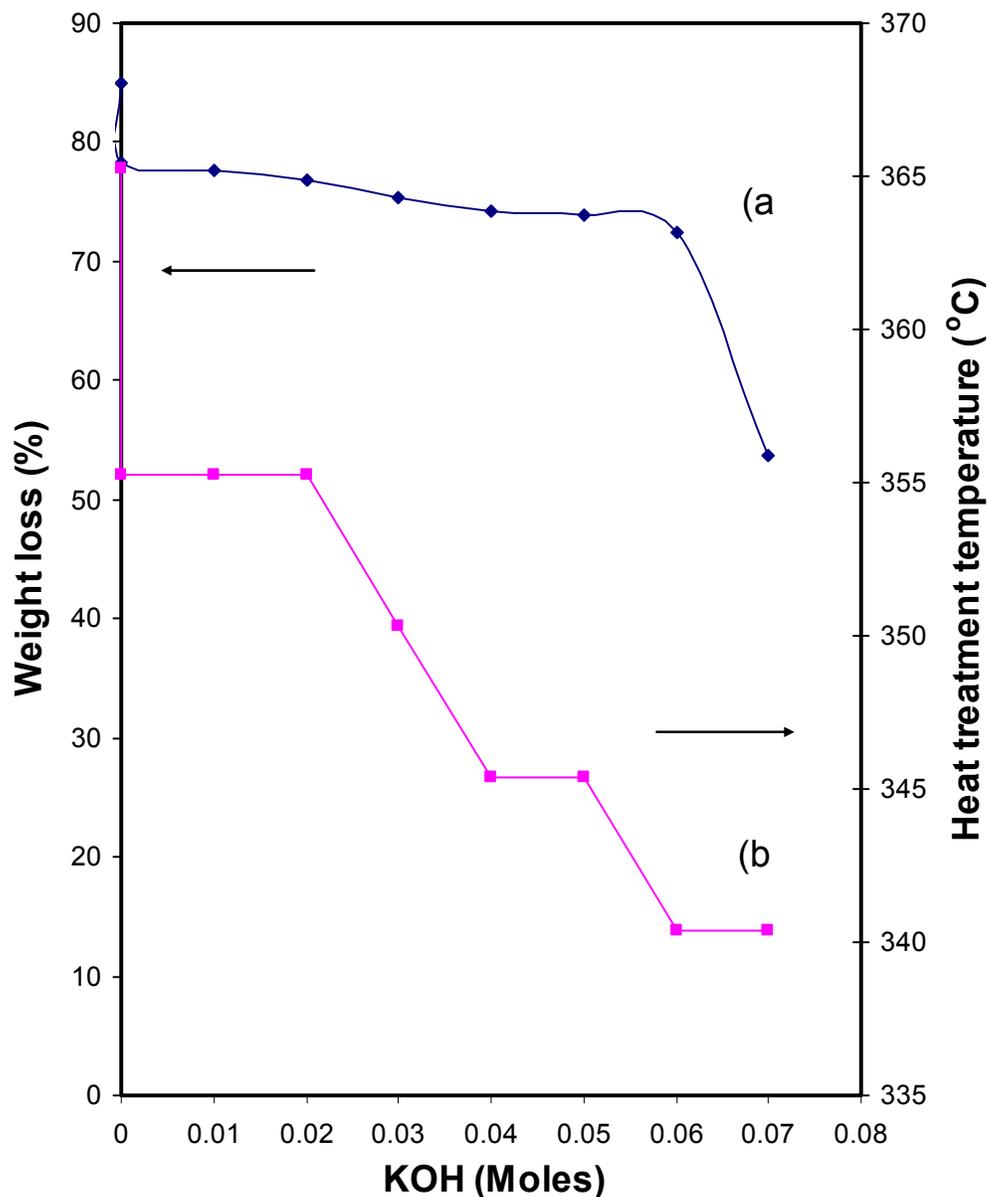


Figure 2: Variation of weight loss % and the peak position of the maximum rate of weight loss as a function of KOH concentration from 0 to 0.07M, taken, from Figure 1.

The data in Figure 1(b) shows that there are two sets of peaks that represent the occurrence of a rapid rate of weight loss in the temperature ranges from 60 °C to 120 °C and 270 °C to 370 °C. The rapid process in the first range is associated with water and moisture evaporation from the samples and the data indicates that the treatment has enhanced such a process. The KOH treatment applied on the SACG from the oil palm empty fruit bunch also gave a similar effect in this temperature range [4]. The peaks in the second range represent a rapid rate of the SACG decomposition or thermal

degradation of the cellulosic structure. The treatment seems to shift the position of these peaks to slightly lower temperatures (as illustrated in Figure 2 (b)), and also produce the overall trend that the height of these peaks is higher for the treated samples. Therefore these data seem to reveal that the KOH treatment can promote the thermal decomposition of the SACG to occur at slightly lower temperature with a more rapid rate.

Figure 3 shows the X-ray diffraction intensity over an angular range from 2.3° to 60° for carbon pellets produced from the untreated SACG pellets by carbonization up to different temperatures from 500 °C to 1000 °C. A similar pattern of X-ray diffraction intensities were observed for the carbon pellets samples (1000 °C) from the treated SACG (not shown here). In both cases the intensities consist of two broad diffraction peaks, i.e. (002) and (100) peaks which lie at approximately from 23.3° to 24.2° and 44.1° to 44.9° respectively. This pattern of diffraction represents the structure of the turbostratic model, which assumes that the samples consist of crystallites that are made up from graphite-like carbon layers[13].

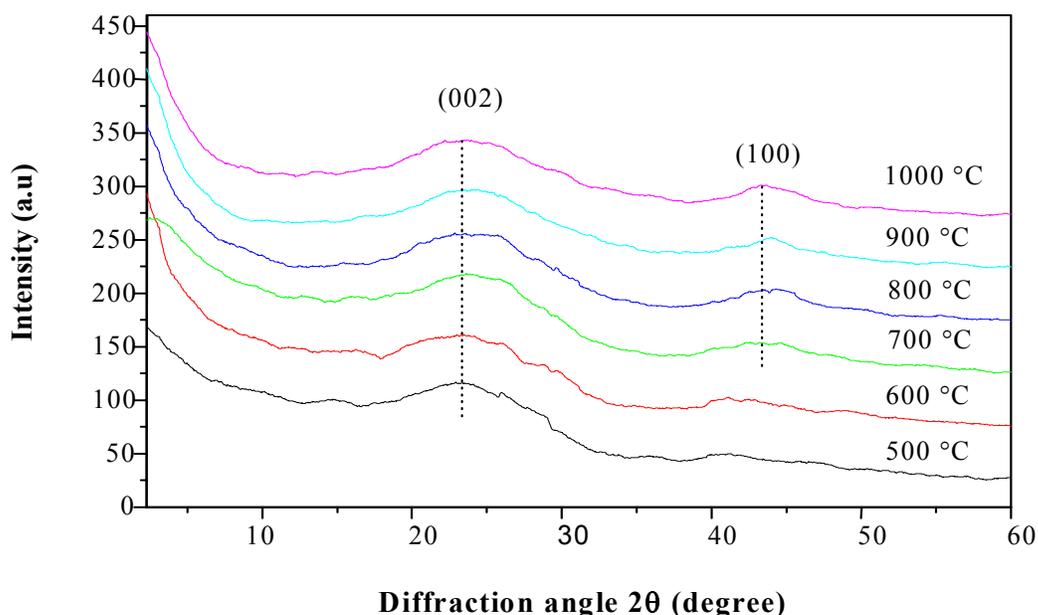


Figure 3: X-ray diffraction for carbon pellets carbonized at different carbonization temperatures from 500°C to 1000°C.

The interlayer spacing  $d_{002}$ , determined from the (002) peak using Bragg equation, and  $L_c$  and  $L_a$  determined from the (002) and (100) peaks respectively using equation (1) are shown in Tables 1 and 2. The data in this table clearly shows that as the carbonization increases, higher growth of crystallites of the carbon pellets from the untreated SACG occurs in the direction of graphitic layers compared to that in the direction of the stack height,  $L_c$ . However, for the carbon pellets (1000°C), the crystallites become smaller as the KOH concentration increases, particularly their stack width. These data shows that the carbonization temperature and KOH treatment gives a contrary effect on the trend of the dimensional change of the crystallites.

Table 1:  $d_{002}$  (Å),  $L_c$  (Å) and  $L_a$  (Å) of carbon pellets from the untreated SACG as a function of carbonization temperatures (CT).

<b>Sample Code</b>	<b>CT (°C)</b>	<b><math>d_{002}</math> (Å)</b>	<b><math>L_a</math> (Å)</b>	<b><math>L_c</math> (Å)</b>
C5	500	3.81	09.93	06.5
C6	600	3.81	09.19	07.0
C7	700	3.82	20.9	08.6
C8	800	3.74	23.10	09.1
C9	900	3.73	25.27	09.4
C10	1000	3.70	27.57	10.3

Table 2:  $L_c$  (Å),  $L_a$  (Å) and  $d_{002}$  (Å) for the carbon pellets from the treated SACG (0-0.07 M KOH) (1000°C)

<b>Sample Code</b>	<b><math>d_{002}</math> (Å)</b>	<b><math>L_a</math> (Å)</b>	<b><math>L_c</math> (Å)</b>
C00	3.73	25.04	10.84
C01	3.74	24.43	10.52
C02	3.75	23.83	10.20
C03	3.76	23.22	09.88
C04	3.77	22.62	09.55
C05	3.78	22.02	09.23
C06	3.79	21.41	08.91
C07	3.80	20.81	08.59

The  $d_{002}$  and  $L_a$  data can be further analyzed using an expression that relates the  $d_{002}$  and  $1/L_a$  through a linear function proposed by Takahashi et al. (1965) [5], i.e.,

$$d_{002} = \alpha_1 + \alpha_2/L_a$$

where  $\alpha_1$  must take the value of around 3.354 and  $\alpha_2$  must be obtained by fitting this equation to the data. The plot of the  $d_{002}$  versus  $1/L_a$  using the data in Tables 1 and 2 are shown in Figures 4 and 5 respectively. The fitting of this equation was made and it was found that  $\alpha_1$  equal to 3.353 and 3.354, and  $\alpha_2$  equal to 9.44 and 9.36 for the carbon pellets from the untreated and treated SACG respectively. The fit seems to be

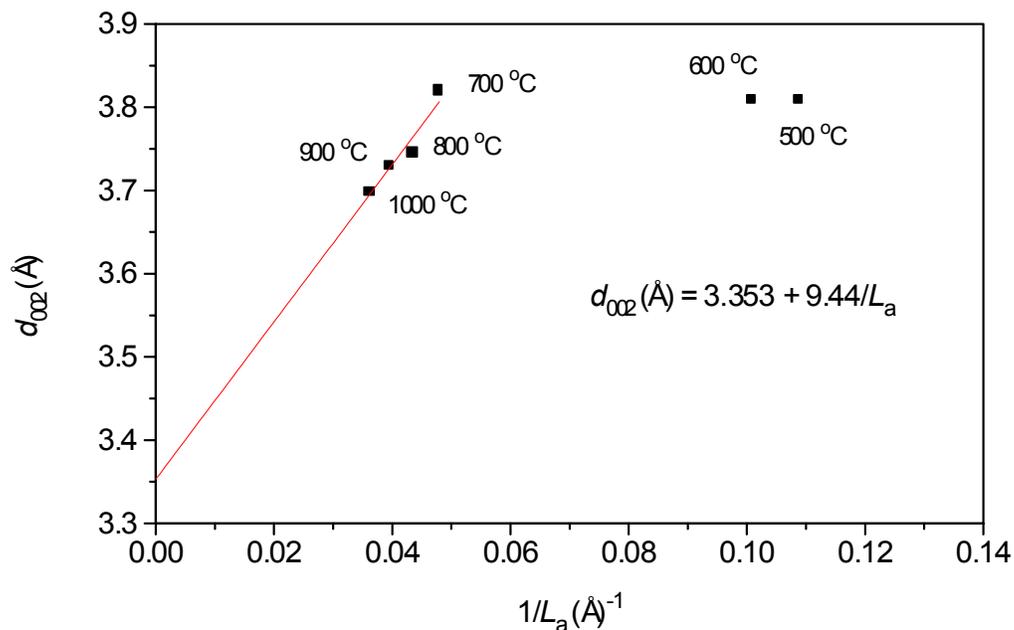


Figure 4:  $d_{002}$  versus  $1/L_a$  for the carbon pellets from the untreated SACG carbonized at temperatures from 500 to 1000 °C

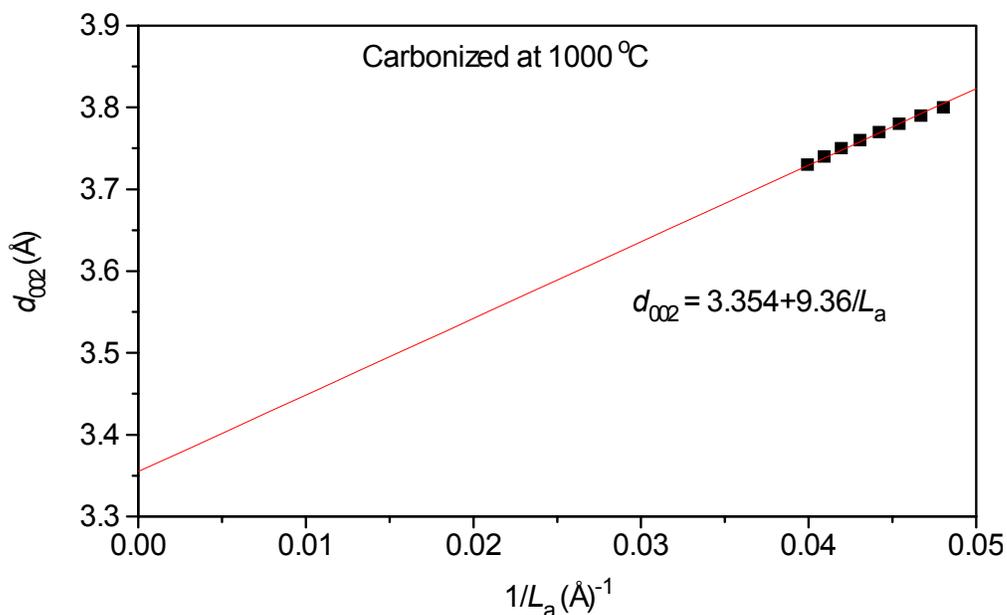


Figure 5:  $d_{002}$  versus  $1/L_a$  for the carbon pellets (1000°C) from the treated SACG

very good for almost all of the data points, except for the data at 500 °C and 600 °C. The reason for this is that at these two temperatures, the turbostratic structure is not yet fully developed, as revealed by the weak (100)-peaks in the X-ray diffraction data (Figure 3). The good agreement in such a fitting indicates that the equation proposed is applicable for the analysis of this type of turbostratic carbon. These results demonstrate the trend

that the changes of the interlayer spacing and the stack width of the crystallite in the samples is not independent of each other because they are both changing systematically during carbonization process.

## CONCLUSION

The thermogravimetry and differential thermogravimetry analysis found that increasing KOH concentration for the treatment of the SACG caused the weight loss of carbon pellets to decrease and the maximum rate of weight loss to increase and this maximum occurs at lower temperature. X-ray diffraction analysis found that the interlayer spacing and dimension of crystallites in carbon pellets from the untreated SACG decreased and increased with the increasing carbonization temperature respectively. For carbon pellets prepared from the carbonization (1000°C) of the SACG treated with KOH (0.0 to 0.07 M), a contrary trend was however observed on the variation of these parameters against the increasing molarity. X-ray diffraction analysis also found that there is a linear relationship between interlayer spacing and  $1/L_a$ . It can be concluded that the KOH treatment on the SACG gave systematic effects on the variation of the weight loss, rate of weight loss, dimensional change of the pellets, and interlayer spacing and dimension of the crystallites during carbonization.

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