

THE EFFECT OF K_2CO_3 TREATMENT ON SELF-ADHESIVE CARBON GRAIN PREPARED FROM OIL PALM EMPTY FRUIT BUNCH

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ABSTRACT

Self-Adhesive Carbon Grains (SACG) is carbon powder that can be compacted into shaped by a compression moulding technique without adding any binder. A low temperature pre-carbonization process was used to prepare SACG from oil palm empty fruit bunch. SACG were ball milled for 36 hours and sieved to obtain powder with particle size less than 53 micron. SACG were then treated with different concentration of K_2CO_3 . The mixture was dried in oven at $110^\circ C$ for 24 hours. The effect of K_2CO_3 treatment on SACG has been investigated by thermogravimetric analyzer (TGA), Fourier transform-infra red (FTIR) and CHNO (carbon, hydrogen, nitrogen and oxygen) analysis. The thermogravimetric analysis showed that the addition of K_2CO_3 in SACG has progressively promoted the pyrolysis and accelerated the dehydrogenation of the treated sample at much lower temperature. The FTIR analysis on the treated SACG found that the peak intensity of carboxyl $C = O$ and $= C - H$ bands decreased as the concentration of K_2CO_3 increased. The CHNO analysis showed that the present of K_2CO_3 in the SACG caused a small change in the elemental composition of the mixture. However, the above results indicate that the K_2CO_3 treatment has changed the thermal characteristic and chemical structure of the SACG.

INTRODUCTION

There are as many reasons to call carbon a conventional material as there are to consider it an advanced one. Over the last three decades industry has played a leading role in the utilization of conventional carbon materials. There are various types of carbon materials that can be found in industry and laboratory such as graphite, diamonds, carbines, fullerene, fibers of carbon and graphite, solid carbons, glassy carbons, carbon black, nanoparticles carbon, carbon nanotubes and multiwall carbon spheres.

These commercial carbon materials are commonly produced from organic materials such as petroleum, coal, polymer, hydrocarbon gas and biomass. Recent research development in United State, Japan and Europe found that lignocellulosic material from biomass has a high potential to be an alternative material to the petroleum based precursor for the production of carbon products. Examples of biomass that has been

widely used to produce carbon are oil palm stone [1,2], oil palm shell [3,4], oil palm fibre [5], coconut shell [3,6,7], almond shell [3] and walnut shell [3,8].

Malaysia is the world largest producer of palm oil and one of the major by-products from oil palm industry is empty fruit bunch (EFB). Its continuous at palm oil mills and annual production approximately amounted to 8.5 million tones makes it attractive for commercial exploitation [9]. EFB has traditionally been used commercially as boiler fuel, mulching materials in the oil palm plantation and organic fertilizer (after burning). However, numerous research efforts have been made to widen its usage as a starting material for making different types of products including roof tiles [10], pulp and paper [11], fiberboard [12] and solid carbon [13-18].

EFB was found suitable to be converted, by a pre-carbonization process, into self-adhesive carbon grains (SACG) that can be pelletized without using any binding agent [15]. A number of attempts have been made in order to further improve the property of solid carbon product prepared from SACG [12-18]. It should be noted here that solid carbon product is widely used in Malaysia, where its imported quantity from 1995 to early 2000 is amounted to RM 117 millions [18]. In the present study, SACG were treated with K_2CO_3 of different concentrations, aiming of investigating the effects of K_2CO_3 treatments toward the thermal characteristics, chemical structure and elemental composition of the SACG.

MATERIALS AND METHODS

EFB were pre-carbonized by a low temperature carbonization process based on the method previously reported [3]. The pre-carbonized EFB was ball milled for 36 hours and sieved in order to obtain SACG powder with sizes less than 53 micron. SACG, designated as samples A, B, C, D, E and F were treated with K_2CO_3 at the concentration range of 0, 1, 3, 5, 7 and 9% by weight respectively. SACG was mixed with K_2CO_3 in 100 cm³ of distilled water using a magnetic stirrer for 1 hour at room temperature before it was dried in an oven kept at 110°C for 24 hour [3,19-21]. The mixture was ball milled again for 20 minutes to produce a fine powder which can pass through a 53 micron sieve.

TG-Shimadzu 501 instrument was used to study the carbonization behavior of the samples (up to 600°C). Heating rates of 20°C/min and nitrogen atmospheres were employed. The chemical structure of the sample was analyzed by FTIR spectrometer (Biorad FTS 1653720). Samples for FTIR were prepared by grinding the sample together with potassium bromide (KBr) and pressed into thin pellets. They were then placed in the sample holder and scanned within the absorption band of 4000 to 400 cm⁻¹. Thermo Finnigan (Eager 300 EA1112) instrument was used for the analysis of CHNO (carbon, hydrogen, nitrogen and oxygen) in the samples.

RESULTS AND DISCUSSION

Figure 1 shows the results of the TG analysis carried out from 20-600°C under an inert (N_2) atmosphere. An initial weight loss occur from 25 to 150°C corresponds to loss of adsorbed water. Polymer decomposition in the SACG is indicated by weight loss beginning at 200°C where the hemicellulose component begins to break down. The rate of change in weight loss reaches a maximum at 300°C as the cellulose and lignin decompose. At that temperature the cellulose has largely decomposed while the lignin components continue to break down. Further heat treatment to 600°C yielded 36-41% solid carbon [3, 22].

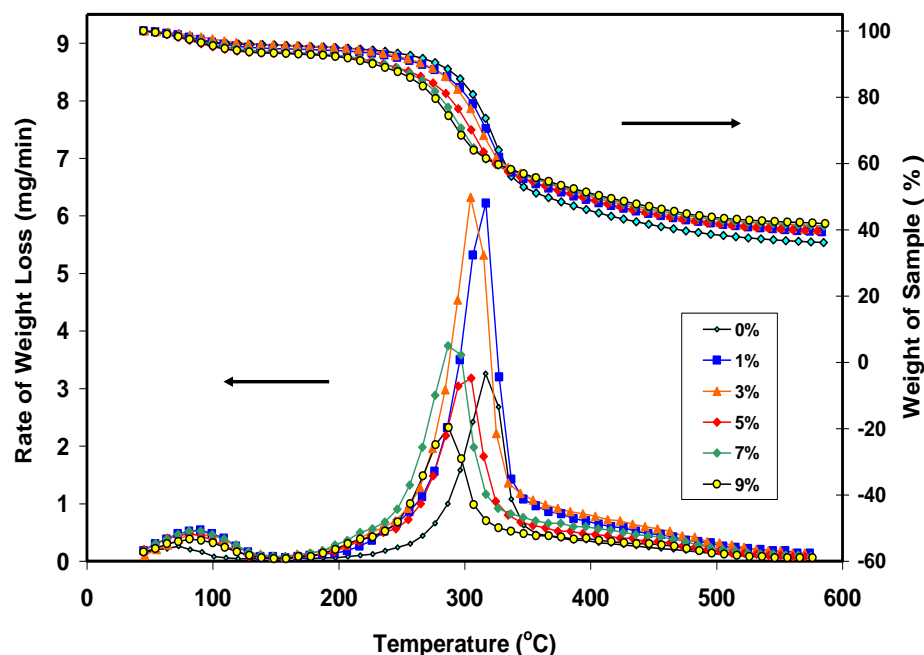


Figure 1 : Thermogravimetry Profiles of the Samples A, B, C, D, E and F.

As can be seen in Figure 1, as the treatment concentration increased the main peak height and position of the rate of weight loss decrease and shift to the lower temperature range. These results suggest, the dehydrogenation of the treated sample started at a lower temperature with the addition of K_2CO_3 , indicating that the treatment has changed the thermal property of the SACG.

A linear behavior has also been observed on carbon prepared from lignin [19] and hydrocarbon [23] with the addition of alkali metal compounds. Recent studies on the carbon prepared from iodine treated SACG [14] and acid treated SACG [17] also found a similar observation on thermal behavior with the SACG carbon produced in the present study.

The distinct thermogravimetric behavior of the untreated and treated SACG may be attributed to the following interactions [7]. First, the more rapid carbonization (200-

250°C) of the treated sample may be the result of partial reaction of the salt with the cellulose in the SACG, for example:



The second weight loss (250-300°C) observed after carbonization in the treated sample could be attributed to CO₂ produced by salt decomposition, which may effect gasification of the already carbonized SACG:



It is also possible that KOH formed at the surface according to reaction (1), decomposed, producing water that also contributes to gasification:



Figure 2 shows the FTIR spectra for the samples A, B, C, D, E and F, whilst the absorption band of FTIR spectrum of each samples are summarizes in Table 1. The broad peak observed at 3400-3200 cm⁻¹ (P1) for each sample is due to the absorption of the hydroxyl group (O-H) [25]. This showed that this group remained in the structure even the SACG is treated at higher concentration.

The peak at P3 (1715 – 1695 cm⁻¹) corresponded to the carboxyl C = O stretching [25]. The peak intensity is slightly decreased as the concentration of K₂CO₃ increased. The decrease of this peak means that most of this functional group was removed as CO₂ to the gas phase and this phenomenon mainly accured up to a treatment temperature of 600°C [26]. Peak at P5 (1550 – 1510 cm⁻¹) is due to the aromatic ring vibration (= C – H). The peaks began to disappear as the K₂CO₃ intake increased. This implied the formation of the carbon aromatic ring from lignin structure in sample E and F [27].

Table 1 : Position of absorption peaks from FTIR spectra for the samples A, B, C, D, E and F.

| Label | Wave Number (cm^{-1}) | Band Origin |
|-------|----------------------------------|---------------------------------|
| P1 | 3400 – 3200 | O – H stretching |
| P2 | 2936 – 2916 | C – H stretching |
| P3 | 1715 – 1695 | C = O stretching |
| P4 | 1650 – 1550 | C = C stretching |
| P5 | 1550 – 1510 | aromatic ring vibration = C – H |
| P6 | 1380 – 1370 | C – H bend |
| P7 | 1250 – 1020 | C – O stretching |

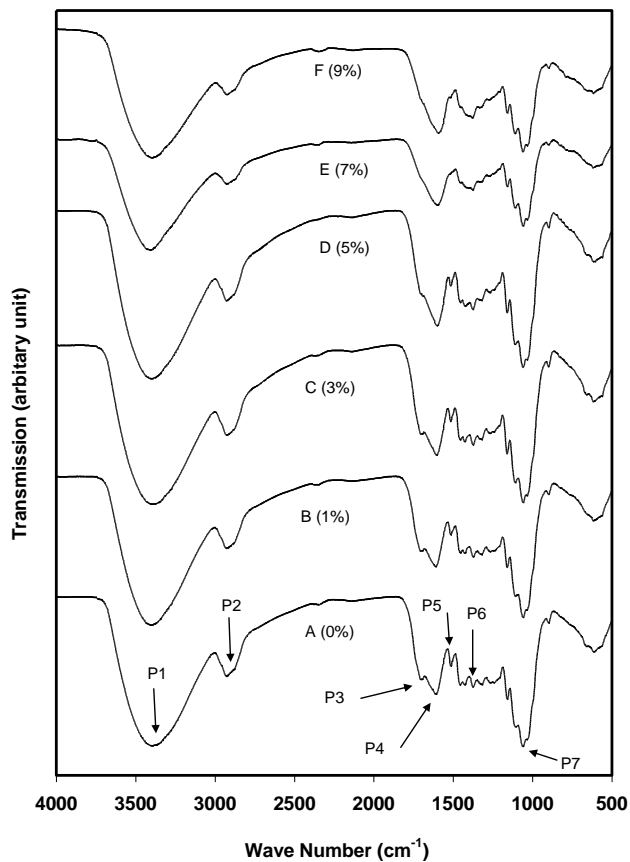


Figure 2 : FTIR Spectra of the samples A, B, C, D, E and F.

Table 2 : Elemental analysis of carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) of the samples A, B, C, D, E and F.

| Sample / composition | C (%) | H (%) | N (%) | O (%) | H/C |
|----------------------|-------|-------|-------|-------|------|
| A (0%) | 52.14 | 6.10 | 0.08 | 41.68 | 0.12 |
| B (1%) | 52.21 | 5.94 | 0.34 | 41.51 | 0.11 |
| C (3%) | 50.81 | 5.49 | 0.01 | 43.69 | 0.11 |
| D (5%) | 49.47 | 6.21 | 0.16 | 44.17 | 0.13 |
| E (7%) | 47.10 | 5.19 | 0.02 | 47.70 | 0.11 |
| F (9%) | 45.86 | 5.47 | 0.03 | 48.64 | 0.12 |

Table 2 shows the elemental analysis of carbon, hydrogen, nitrogen and oxygen of the samples A, B, C, D, E and F. The results in this table shows that the carbon and hydrogen contents slightly decreased with increasing concentration of K_2CO_3 , where as oxygen content appears to increase slightly and nitrogen content changes unsystematically. It is possible that 1 to 9% addition of K_2CO_3 is too small quantity to change significantly the percentage of elemental composition in the sample.

CONCLUSION

The TGA results showed that the increase in K_2CO_3 concentration in the SACG causes the main peak height and position of the rate of weight loss to decrease and shift to the lower temperature region. Therefore, it can be concluded that the addition of K_2CO_3 in the SACG has promoted the pyrolysis and dehydrogenation process of the treated sample toward much lower temperatures. The FTIR analysis found that the peak corresponded to the carboxyl $C = O$ and $= C - H$ progressively disappear as the K_2CO_3 intake increased. This indicates that the K_2CO_3 treatment has changed the chemical structure of the SACG. The CHNO analysis showed that the treatment gave insignificant effect on the elemental composition, probably due to the insufficient amount of the K_2CO_3 used. These results demonstrate that the property of SACG can easily be modified and these informations are useful for studying the processing of the SACG pellet into carbon pellet by a carbonization method.

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