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Research Article

Highly Porous Carbon Materials from Biomass by Chemical and Carbonization Method: A Comparison Study

Wan Nor Roslam Wan Isahak, Mohamed Wahab Mahamed Hisham, and Mohd Ambar Yarmo

Low Carbon Economy (LCE) Research Group, School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia (UKM), 43600 UKM Bangi, Selangor, Malaysia

Correspondence should be addressed to Wan Nor Roslam Wan Isahak; wannorroslam@yahoo.com

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Porous carbon obtained by dehydrating agent, concentrated sulfuric acid (H_2SO_4), from biomass containing high cellulose (filter paper (FP), bamboo waste, and empty fruit bunches (EFB)) shows very high surface area and better thermal behavior. At room temperature (without heating), treatment of H_2SO_4 removed all the water molecules in the biomass and left the porous carbon without emitting any gaseous byproducts. Brunauer-Emmett-Teller (BET) surface analysis has shown that bamboo-based carbon has good properties with higher surface area (507.8 m^2/g), micropore area (393.3 m^2/g), and better thermal behavior (compared to FP and EFB) without any activation or treatment process. By acid treatment of biomass, it was shown that higher carbon composition obtained from FP (85.30%), bamboo (77.72%), and EFB (76.55%) is compared to carbon from carbonization process. Under optimal sulfuric acid (20 wt.%) uses, high carbon yield has been achieved for FP (47.85 wt.%), bamboo (62.4 wt.%), and EFB (55.4 wt.%).

1. Introduction

Biomass is a renewable resource that provided steady and abundant supply of waste materials such as empty fruit bunch (EFB), wood chips, and bamboo. These waste materials are traditionally used for the production of charcoals and carbon materials including the porous structure activated carbons and microporous amorphous carbon materials that are widely used as adsorbents [1–3], materials for the separation of gases [4–7], and catalyst support [8, 9]. On the other hand, there is growing interest in the development of new carbon materials produced directly from plant materials to make carbon composites [10], carbon nanotubes (CNTs) [11, 12], and environmental adsorbents [13, 14].

Carbon materials with a developed porous structure such as activated carbon, coke, and charcoal are produced by pyrolysis or carbonization of the biomass followed by physical and chemical activation. In carbonization of wood to produce charcoal, other side products, namely, carbon monoxide (CO), methane, and water are obtained [10]. Carbonization process of wood at about 400°C could yield 19% charcoal by weight (%). Considering of biomass and charcoal compositions, it is estimated theoretical yield of high-quality charcoal could be produced as much as 44 to 55%. Tippayawong et al. [15] reported that the carbonization of wood in a small natural draft carbonizer gives charcoal yield of 33–38%. In 1990s, Mok et al. (1992) have reported the charcoal production by using sealed reactor. The biomass bamboo type *Eucalyptus gummifera* was pyrolyzed at typical condition to obtain about 48% of charcoal [16]. In addition, different species of biomass feedstock would influence the charcoal production and quality. Higher charcoal yields were obtained from biomass species that contains high lignin or low hemicelluloses content.

Generally, the carbonization of biomass would lead to produce charcoal as well as gaseous products such as CO, CH_4, and water as shown in (1) [10]. This process seems unfriendly approach for charcoal synthesis in terms of higher greenhouse gas (CHG) emissions. In this paper, we present the properties of carbon materials produced by dehydration method (chemical method) based on high cellulose content sources expressed by (2). Theoretically, by dehydration

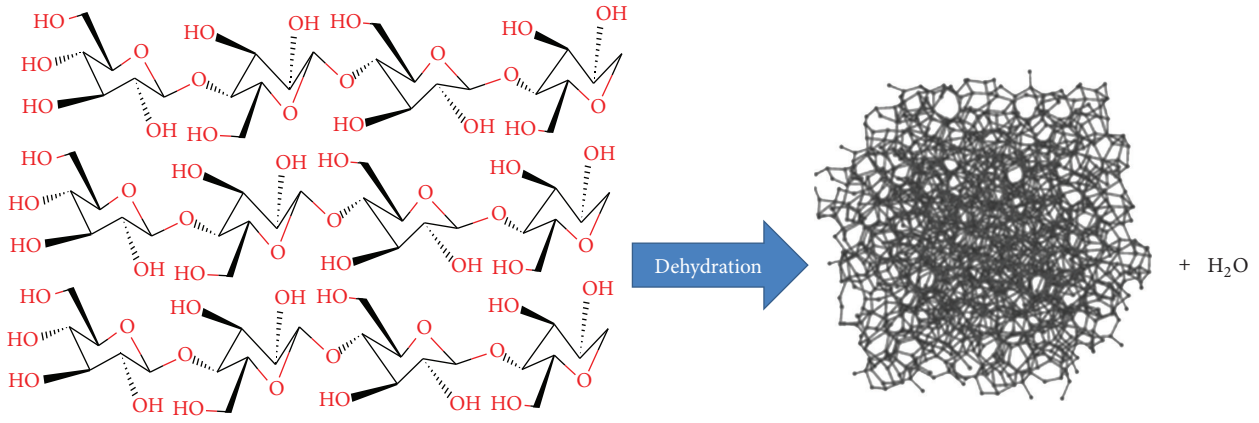

Figure 1: Transformation of biomass containing high cellulose into porous carbon by dehydration (chemical method).

process (chemical method) of cellulose, 5 moles of water in cellulose structures can be removed by concentrated sulfuric acid to form porous carbon. Figure 1 illustrated the dehydration of cellulose into porous carbon. This is a green route to synthesis of high content of carbon without any GHG emissions which only produced water as a byproduct as would be explained in this paper:

$$\underset{\text{(Wood)}}{C_{21}H_{32}O_{14}} \xrightarrow[\text{heat}]{} \underset{\text{(Charcoal)}}{C_7H_4O} + \underset{\text{(GHG gasses)}}{9CO + 5CH_4} + \underset{\text{(Water)}}{4H_2O} \quad (1)$$

$$\underset{\text{(Cellulose)}}{(C_6H_{10}O_5)_n} \xrightarrow{\text{Dehydration}} \underset{\text{(Carbon)}}{6_nC} + \underset{\text{(Water)}}{5_nH_2O} \quad (2)$$

In this work, a comparison study was drawn based on the types of biomass using carbonization and dehydration process (chemical) to produce porous carbon. To find better solution to environmental issues, the dehydration process was applied as an alternative technique to synthesis of high-yield and -quality carbon at room temperature (without heating) which is a very low-cost route, easy in handling, and zero emission of GHG. This study was focusing on three selected high cellulose content of biomass samples, namely, bamboo, EFB, and filter paper (FP). complete physical characteristics and properties of synthesized carbon were also studied throughout this paper.

2. Experimental and Analysis Methods

2.1. Sample Preparation. Three high cellulose contents or biomass samples, namely, bamboo, FP (Whatman no. 1), and EFB were selected as potential sources. The EFB and bamboo were obtained from local palm oil farm and furniture factory in Kelantan, Malaysia, respectively. These collected samples were washed thoroughly with distilled water to remove adhering soil and dust and dried at 110°C overnight. The FP (Whatman no. 1) was purchased from GE Healthcare Limited, UK. Analytical grade sulfuric acid (98 wt.%) was supplied by Fisher Scientific Limited, UK.

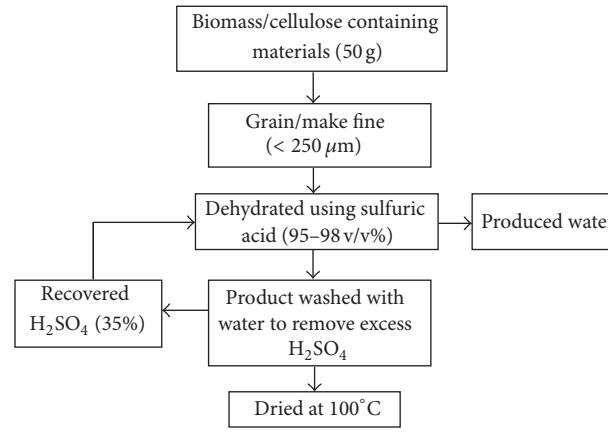

Figure 2: Flowchart for carbon production from high cellulose content materials.

2.2. Preparation of Porous Carbon

2.2.1. Carbonization/Heating Method. The high cellulose content feedstock (Whatman FP: type no. 1, EFB, and bamboo) were dried at 110°C for 12 h [17]. Then, samples was carbonized in nitrogen at 500°C for 2 h by a ramping temperature of 6°C/min.

2.2.2. Dehydration Process. 50 g of high cellulose content feedstock (bamboo, FP, and EFB) were putted in a proper quartz column. Then, 15 mL of sulfuric acid (H_2SO_4) was flowing through the column. The fast reaction was performed at room temperature. The flowchart of this work was summarized in Figure 2.

2.3. Physical and Chemical Characterization. Nitrogen adsorption at 77 K (liquid nitrogen) was conducted using a Micromeritics ASAP 2010 instrument to obtain the adsorption isotherm of each sample. The Brunauer-Emmett-Teller (BET) surface area, micropore volume, and micropore

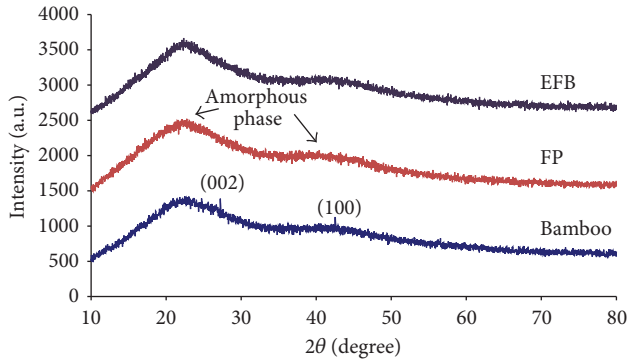

Figure 3: XRD diffractogram of carbon (bamboo, FP, and EFB) synthesized by dehydration process.

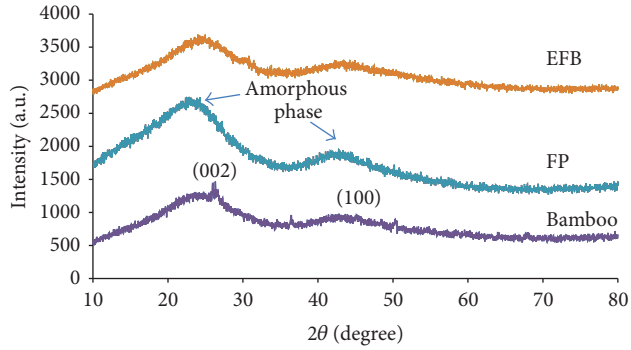

Figure 4: XRD diffractogram of carbon (bamboo, FP, and EFB) synthesized by carbonization process.

area were calculated from the isotherms. Before running analysis, the samples were degassed at 350°C for 6 hours. The crystallinity analyses of the samples were performed using Bruker DB-Advance X-ray diffractometer (XRD), Germany. The analyses were employing Cu Kα radiation at 2θ ranging from 10° to 80° of 1 g sample. The infrared spectra of the carbon samples were recorded on a spectrum 400, FT-IR/FT-NIR spectrometer (Perkin Elmer, UK) using the attenuated total reflection (ATR) method for sample preparation technique. A mass of 0.5 mg of carbon sample was used for all tests. Elemental analyses were carried out using a Fison EA 1108 C, H, N, O analyzer. The surface micrograph of porous carbon was studied using field emission scanning electron microscope (FESEM). The oxidative mass loss of the samples was analyzed in air using dynamic thermal gravimetric analysis (TGA) with a simultaneous TGA-DTG system (Model: Mettler Toledo). To reduce the influence of the sample quantity on the analyses, 5 (±0.2) mg of each sample was used in each analysis and a constant air flow of 50.0 mL min^{-1} was maintained throughout the entire process. To minimize possible differences in the moisture content between samples, all TGA samples were equilibrated at 50°C for 5 min before heated to 700°C at a ramping rate of 5°C min^{-1}.

Table 1: Surface properties of carbon from different biomass.

Physical properties	Dehydration method			Carbonization method		
	FP	EFB	Bamboo	FP	EFB	Bamboo
Surface area (m^2/g)	376.93	446.27	507.76	153.00	263.24	293.46
Micropore area (m^2/g)	270.28	359.54	393.29	115.00	223.42	234.72
Micropore volume (cm^3/g)	0.17	0.19	0.21	0.06	0.10	0.12

Table 2: Elemental composition (wt.%) in various biomass.

Biomass source	C	H	O	N
Filter paper (wood-based)	40.83	6.79	42.14	10.24
Bamboo	36.32	3.88	48.74	11.06
Empty fruit bunch (EFB)	35.65	3.97	48.03	12.35

3. Results and Discussion

3.1. Surface and Porosity Studies. Surface analysis by BET showed that the carbon synthesized by dehydration method had better surface properties in terms of surface area and micropore area compared to carbonization method. It is clearly shown that the carbon prepared by dehydration using sulfuric acid is higher in surface area and porosity. This could be a good indication of the sulfuric acid functioning as a water removal which not much breaks cellulose walls. Bamboo feedstock gave better properties of carbon with higher surface area (507.8 m^2/g), micropore area (393.3 m^2/g) and micropore volume (0.21 cm^3/g). FP has showed lower surface area (376.9 m^2/g) and porosity (270.28 m^2/g) as summarized in Table 1, without any activation and treatment process. It indicates that the bamboo type of biomass is composed of high content of ash component compared to FP and EFB sources. High-ash content biomass functions as a precursor to form high porosity carbon materials [18, 19]. In further work, this carbon (from dehydration or carbonization) can be activated by chemical and physical methods to increase their surface area up to 2500 m^2/g. In literature, Zhang et al. were reported the synthesis of very high-porosity carbon-derived rice straw and corn stalks after chemical activation with potassium hydroxide (KOH) [20, 21].

3.2. Crystallinity. The XRD analyses show that the carbon synthesized from bamboo, EFB, and FP were clearly formed in an amorphous state. The crystalline phase of high content cellulose is broken by sulfuric acid to form amorphous carbon. There are two obvious peaks represent amorphous carbon at 2θ value of 22.4° and 42.3° as shown in Figure 3. The appearance of sulfuric acid together with high cellulose content feedstock could pick up the water molecule from samples to form high purity and porosity carbon. No any significant difference between EFB, FP, and bamboo synthesized by dehydration and carbonization process (Figure 4). XRD pattern matches well to previously reported pattern for

Table 3: Elemental composition (value in wt.%) in biomass-based carbon.

Elements	Carbonization method			Dehydration method			Commercial charcoal (CC)	Lignite (coal)
	FP	Bamboo	EFB	FP	Bamboo	EFB		
C	84.2	74.58	71.43	85.30	77.72	76.55	73.60	60–75
H	3.62	2.26	2.54	4.46	3.82	3.17	4.82	6.0–5.8
N	0.31	0.82	1.47	0.21	1.10	1.1	1.4	34–17
Volatile elements	11.87	22.34	24.56	9.89	17.36	19.18	20.18	45–65

Table 4: Carbon yields from acid treatment (dehydration) of high cellulose content.

Quantity of H_2SO_4 uses (wt.%)	Carbon yield (wt.%)		
	FP	Bamboo	EFB
5	32.5	41.0	35.6
10	42.3	48.5	43.2
15	44.6	56.4	45.5
20	47.9	62.4	55.4

nongraphitic carbon [22]. However, little amount of graphite phase is detected in bamboo-based carbon approximate at 27.2° and 44.5°, respectively, which assigned to the planes of graphite (002) and (100). It was difficult to obtain fully graphite of solid carbon at low carbonization temperatures (such as 500°C).

3.3. Fourier Transform Infrared Spectroscopy (FT-IR) Study. FT-IR analysis of cellulose-rich samples exhibits a typical carbohydrate-type spectrum. The peaks at 900 cm^{-1} to 1200 cm^{-1} are associated with absorption by OH, CH, C–OH, and CH_2 groups in the glycosyl units of cellulose (untreated samples) (Figures 5(a), 5(b), and 5(c)). The bands at 875–750 cm^{-1} are assigned to aromatic C–H group out-of-plane bending vibrations.

The FT-IR spectrum also exhibits bands at 3340 and 2900 cm^{-1} representing stretching vibrations of O–H (hydroxyl or carboxyl) and aliphatic C–H, respectively, whereas the bands at 1725 and 1630 cm^{-1} are attributed to C=O and C=C vibrations, respectively, which supporting the existence of aromatization of sugars structure. After heating at 500°C for 2 hours, it was shown that all of these peaks disappeared due to the complete decomposition of the glycosidic structures. In fact, the identified peaks at 3340 cm^{-1} (O–H), 2900 cm^{-1} (C–H), 1720 cm^{-1} (C=O), and 1630 cm^{-1} (C=C) were diminished during carbonization and dehydration processes.

3.4. Elemental Composition (wt.%) by CHNSO Analyzer. The high cellulose content samples (filter paper, EFB, and bamboo) are composed in the ranging of 35.65–40.83 wt.% (C), 3.88–6.79 wt.% (H), 42.14–48.74 wt.% (O), and 10.24–12.35 wt.% (N) as shown in Table 2. All these samples consist above 50% of cellulose and the rest were hemicelluloses and lignin.

The elemental analysis of porous carbon prepared by carbonization and dehydration processes and, commercial charcoal (CC) is displayed in Table 3. The carbon prepared by dehydration process gives slightly similar carbon content (wt.%) compared to carbon from carbonization process. The H and N content is almost the same for different carbon while, content of volatile elements of carbon prepared by carbonization process is slightly higher than dehydration process. However, the lower value of this element can be achieved by employing the higher carbonization temperature above 500°C. The carbon prepared from dehydration have better properties and carbon content (wt.%) compared to bulk coal and commercial charcoal from market as well as carbon synthesized by carbonization method.

3.5. Surface Micrographs. From FESEM micrographs below (in Figures 6(a) and 6(b)), it was clearly shown that the carbonization and dehydration methods successfully produce highly porous carbon (based on bamboo biomass) without any heating and activation. The micrograph of carbon surface from dehydration method was not that dissimilar to the carbon produced by carbonization method. This means that dehydration by using sulfuric acid can be performed as well as heating (carbonization) at above 500°C.

3.6. Thermal Behavior by TGA. Significant difference in oxidative mass change is observed between the dehydration and carbonization processes of high cellulose content samples. For carbonized carbon from EFB, it is oxidized easier than carbon from bamboo and FP sources. At 450°C, EFB carbon mass is reduced 5 wt.% and FP carbon was starting decomposition at the same conditions. The bamboo-based carbon gives higher mass residue of 85 wt.% at thermal degradation temperature of 700°C as shown in Figure 7.

The comparatively large difference is also observed in the carbon samples prepared by dehydration process. Bamboo carbon has shown good properties of oxidative behavior in terms of higher residue balance of 87 wt.% (Figure 8). It is indicated that bamboo has higher content of lignin compared to FP and EFB. The lignin compound can be functioned for increasing thermal stabilization of carbon [17].

3.7. Effectiveness of Dehydration Process. Comparative studies show that different quantities of sulfuric acid (H_2SO_4) are used for dehydration process of the selected raw materials. The quantity 20 wt.% of H_2SO_4 shows the significant effects on carbon yield (wt.%) for different source high cellulose contents (Table 4). Bamboo source gives higher carbon yield of 62.4 wt.% compared to EFB (55.4 wt.%) and FP (47.9 wt.%). The high-level content of ash in bamboo relatively affects

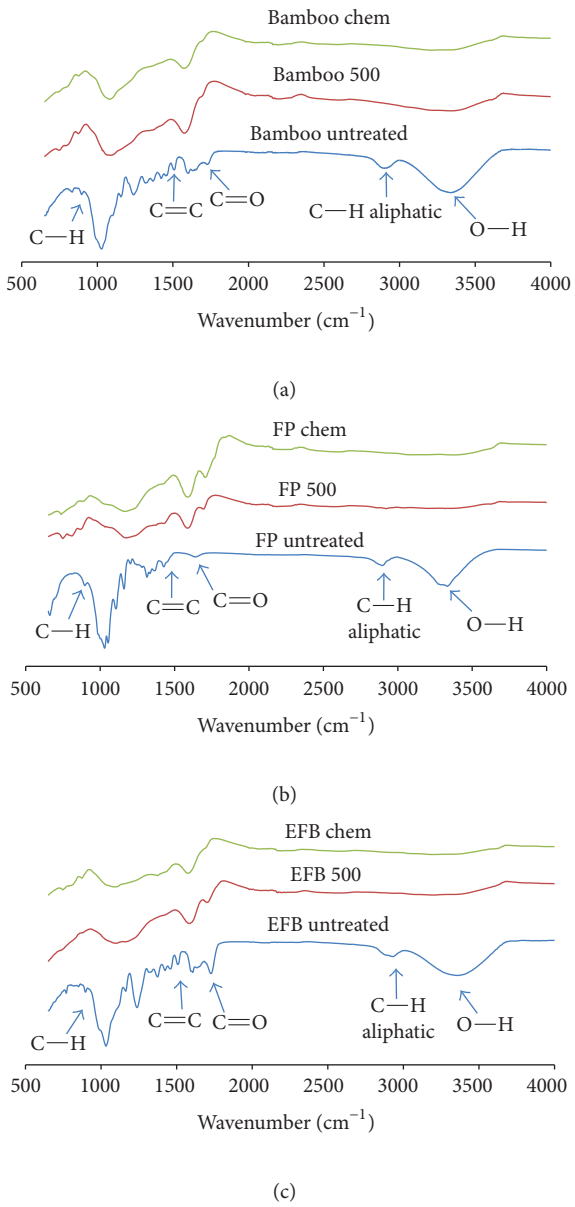

Figure 5: FT-IR spectrums of (a) bamboo, (b) FP, and (c) EFB samples (untreated, heated at 500°C, and chemical dehydration).

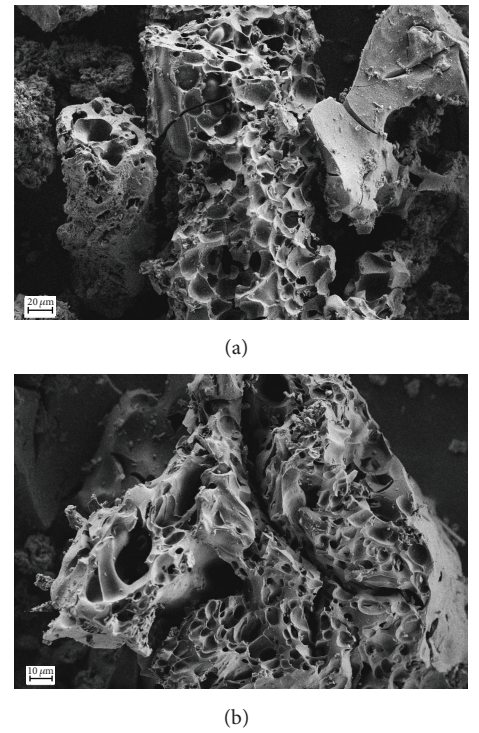

Figure 6: FESEM micrograph for bamboo biomass: (a) carbonization and (b) dehydration (chemical) routes.

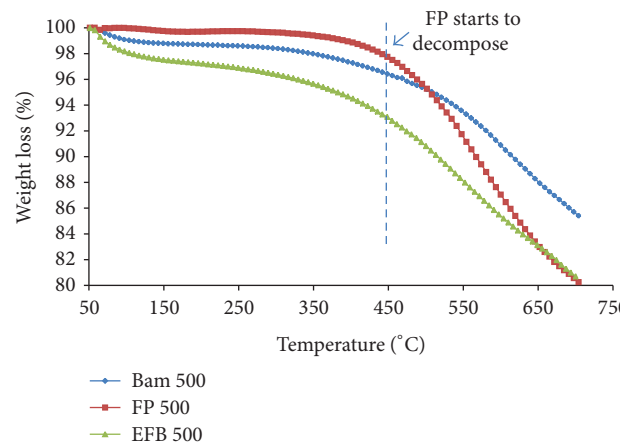

Figure 7: TGA analyses for bamboo, FP, and EFB carbons from carbonization process.

the carbon yield from biomass pyrolysis process [19]. This parameter can stimulate dehydration process of biomass into high content of carbon which has wide potential uses as an absorbent, catalyst, and solid fuel.

4. Summary

These studies show that the porous carbon with better surface area and thermal stability can be produced from filter paper (FP), empty fruit bunches (EFB), and bamboo by dehydration process using concentrated sulfuric acid. It is also shown that better properties and characterization of carbon could be obtained compare with carbonization process. The carbon obtained from these processes exhibited high specific surface area and porosity without emissions of greenhouse gasses (GHG) such as CO_2. This process is expected to stimulate directly decreasing global warming effect, in other way, contributing easier, and green route to produce highly porous carbon materials from biomass waste.

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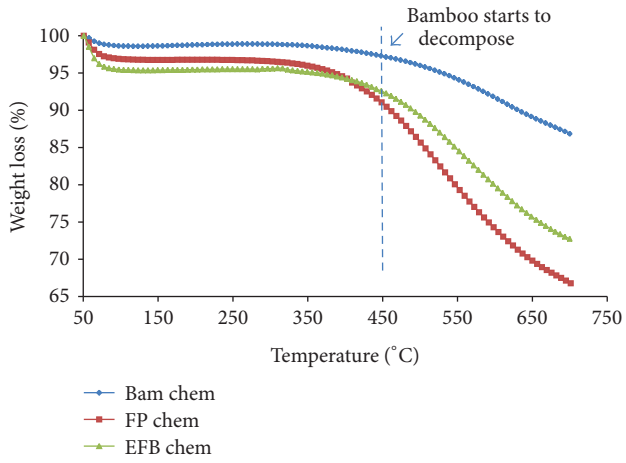

Figure 8: TGA analyses for bamboo, FP, and EFB carbons from dehydration process.

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