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ACTIVATED CARBON PREPARED FROM NATIVE OIL PALM EMPTY FRUIT BUNCH FIBRE

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ABSTRACT

Empty fruit bunch (EFB) fibre is one of the residues generated during Oil palm processing which accounts for the 22% of Fresh Oil Palm Fruit. Thus, potential of the fiber was studied for the production of sustainable activated carbon using Zinc Chloride [$ZnCl_2$] and Phosphoric acid [H_2PO_3] as activating reagents. Surface area and porosity of the activated carbons and the co-pyrolysis of fiber and Low Density Polyethylene (LDPE) at 500°C char products were determined. Thus, both results show that the activated carbon prepared from Zinc chloride has higher surface area and pore volume than Phosphoric acid. Likewise, the surface area and porosity of the co-pyrolysis char product for the fiber and LDPE samples indicated that mixture (20% LDPE and 80%EFB) has the highest BET surface area (597.27m^2/g). Also, the pore sizedistribution of the prepared Activated Carbon (AC) calculated using Density Functional Theory (DFT) method indicated that both Activated carbons as well as the co-pyrolysis char product are in the range of 1.6-2.7 nm using the DFT model plot which show broad peaks in the microporous condition region. So, the fiber can produced high surface area and pore volume activated carbons through pyrolysis as well as through chemical activation.

Keywords: Oil Palm, EFB Fiber, Activated Carbon, Pyrolysis, Char Product

INTRODUCTION

Oil palm (*Elaeis Guineensis*) is a plant that produces oil and it is widely consumed almost all over the world [1]. Oil palm cultivation originated in West Africa, where oil palm trees were originally planted in traditional agricultural production systems along with other annual and perennial crops. Palm oil was said to have been domesticated in Nigeria over the years ago [2]. Palm oil production had increased substantially, and Nigeria had 74 percent of the world's plantations [3]. Globally, the plantations of oil palm increased dramatically in countries like Malaysia and Indonesia, where these two countries contributed about half of the world's total plantation area, and Nigeria produced just over 30 percent [4].

Several streams of waste biomass are generated during its plantation harvesting processes. Empty fruit bunch (EFB), mesocarp fiber (MF), palm kernel shell (PKS), palm kernel meal (PKM), and palm oil mills effluent (POME) are produced from fresh fruit bunches (FFB) [5]. Crude palm oil (CPO) and Palm kernel oil (PKO) are the main products of palm oil processing industry [6]. Similarly, palm oil production at the oil mill abundance of biomass waste materials were generated such as fresh fruit bunch (EFB), Palm oil mill produce 14% fibers, 7% shells and 23% EFB. Empty Fruit Bunch accounts for 19.5 million tons in 2008 [7]. Commercially available activated carbons were prepared from non-renewable and expensive materials, which also contributed to uncontrolled air pollution. Although the fact that it can be produced from any carbonaceous material is true, in the early days, most commercialized activated carbon came from petroleum residues, wood, coal, lignite, and peat [9]. However, these materials have been employed in a wide number of applications on an industrial scale, including purification technologies, the removal of pollutants, and electrochemical devices. As activated carbon can be produced by both naturally occurring and synthetic carbonaceous solid precursors, it has been classified based on its starting material [10]. Thus, production of activated carbon from waste agricultural products, particularly oil palm biomass, has been explored since 1996 [9]. Several studies reported the preparation of activated carbon from various raw materials using $ZnCl_2$, KOH, K_2CO_3 and H_3PO_4 as activating agents [11]. However, no report was observed on the preparation of activated carbon using native palm oil and empty fruit bunch fiber with the above-mentioned activating agents.

Activated carbon is one of the most versatile and useful adsorbents for the removal of pollutants from polluted gases and liquid steam because of its large adsorption capacities, extremely high surface areas, and well developed porous structures, fast adsorption kinetics, and good mechanical properties. Therefore, the development of methods to convert waste materials into useful materials such as activated carbon is a greatly desired effort that offers a sustainable future. Agricultural wastes such as palm oil empty fruit bunches, corncob, coconut shells, and other biomasses are of interest for the preparation of activated carbon due to their availability and being cheap in nature as well as rich in carbon [12]. Activation carbon is a carbon-based material that has been processed to maximize its absorptive properties, yielding a superior adsorbent material. It is also charcoal that has been heated or otherwise treated to increase its absorptive power. It is a highly porous, absorptive carbon used in the removal of colours or impurities [13].

Physical activation involves carbonization followed by activation using carbon (IV) oxide (CO_2) or steam (H_2O), while chemical activation involves using one of the reagents as an activating agent [14]. Thus, the chemical activation process is an efficient method to produce activated carbon with a high surface area and a distributed porosity [15]. Thus, co-pyrolysis of biomass substrate using waste plastics (hydrogen-rich compounds like this) might reduce the coke formation and could decrease the excessive coke development that deactivates the catalyst during the pyrolysis process[16]. A catalytic co-pyrolysis of corn stalk and high density polyethylene (HDPE) over an HZSM-5 zeolite catalyst was studied using quantitative Py-GC/MS to improve aromatic hydrocarbon production. The results showed that the most aromatic hydrocarbons were achieved in the temperature range of 500°C to 600°C. The optimal temperature was observed at 700°C and the aromatic products remained constant when the biomass/HDPE ratio was greater than 1:1, but then increased with a decreasing biomass/HDPE ratio [17].

Co-pyrolysis of red oak and high density polyethylene (HDPE) was conducted using a laboratory-scale continuous fluidized bed reactor at a temperature range of 525 to 675 °C. Three of the pyrolysis products (pyrolysis-oil, non-condensable gases, and char) were analyzed to assess the influence of pyrolysis temperature and co-feeding of biomass with HDPE. The results showed that the pyrolysis temperature (625°C) supported the pyrolysis oil yield 57.6wt %. It was observed that the synergistic effect of plastic and biomass has influenced the higher heating value (36.6 MJ/kg) of the pyrolysis oil, increased the production of furan, acids and water from red oak, inhibited char formation from red oak and improved the HHV of char [20]. Similarly, the char produced from co-pyrolysis had a significantly lower BET surface area than red oak biochar. It was observed that the HDPE-derived particulate matter blocks the pores. The synergetic interaction also resulted in the formation of large and shallow micro-pores on the char surface [18]. This research compares the characteristics of activated carbons prepared from the native EFB fiber using two different activating agents and the char product obtained at the end of the co-pyrolysis process of the fiber with LDPE.

This research was aimed at preparing and characterization of the activated carbon from palm oil empty fruit bunch using zinc chloride and orthophosphoric acid as activating agents. The char carbon from the slow co-pyrolysis of EFB fiber with low density polyethylene (LDPE) plastic was also characterized. Also, to investigate the potential of the fiber for the preparation of activated carbon and provide information on the waste-to-resource conversion process.

MATERIALS AND METHODS

The palm oil empty fruit bunch (EFB) fiber sample was collected from three different palm oil processing plants (Otukpa, Oroken, and Owukpa) in Benue State, Nigeria. Prior to the analyses, the samples were pretreated and kept in an airtight container until required for the analyses. Standard procedures were adopted for the preparation of solutions and other required substances for the analyses, using deionized water as the solvent for the preparation of aqueous solutions. The instruments used for the study were calibrated according to the manufacturer’s instructions. The reagents used for this research were Zinc Chloride (LOBA Chemie 97.0% Purity), Phosphoric acid (BDH 96% Purity), and Nitric acid (BDH 99.9% Purity). A solution of zinc chloride (0.1 mol/dm^3) and a phosphoric acid solution (0.1 mol/dm^3) were prepared [21-22].

Preparation of Activated Carbon

The dried EFB fiber sample was impregnated directly with the H_2PO_3 reagent and labeled EFBP, then impregnated with $ZnCl_2$ and labeled EFBZ. After the impregnation, the samples were kept for 72 hours in the water bath at 80 ^{0}C with constant shaking of 7 rpm to ensure sufficient absorption of the reagents by the sample. The sample was dried in an oven at 110°C for 24 hours after the impregnation. The sample was taken into the Muffle furnace and heated to 200 °C for 15 minutes, then heated to 500 °C for 45 minutes [19]. After the chemical activation, the activated carbon was refluxed with distilled water for 3 hours to remove the remaining reagent. After that, the method was repeated several times to reach a constant pH. After that, it was refluxed with 0.1 M HNO_3 for 1h to remove heavy metals and ash [20].

The Co-pyrolysis Process of EFB fiber and LDPE

EFB fiber and low density polyethylene (LDPE) were co-pyrolyzed at different compositions (100%EFB, 10%LDPE and 90%EFB, 20%LDPE and 80%EFB, 30%LDPE and 70%EFB, 40%LDPE and 60%EFB) using a pyrex glass reactor as shown in [21].

Activated Carbon Characterization

The prepared ACs were characterized using a surface area to determine their surface area and pore volume, BET surface area and morphological studies. The surface area and pore volume of activated carbon (AC) were determined by N_2 adsorption isotherms at 77.35K using the Quantachrome Instrument (Version 11.03). The AC samples were degassed for 3 hours at 250 oC in a vacuum. The surface area was determined using the Multipoint Brunauer-Emmett-Teller (BET) method, while pore volume and pore size were estimated by the application of the Barrett-Joyner-Halenda (BJH) method. The DR method was used to determine the micropore (S_{mi}) surface area. The SEM images were taken using a JEOL JSM-5000V Scanning Electron Microscope [20].

RESULT AND DISCUSSION

The results of the analyses are presented in tables 1 and 2.

Table 1: Surface area properties of the prepared activated carbon

Sample	S_{BET} (m^2/g)	S_{mi}	S_{mi}/ S_{BET}
EFBZ	313.33	369.03	1.178
EFBP	285.02	327.31	1.148

The surface area analysis presented in Table 1, shows the porous properties of the prepared AC, which was found to exhibit a good BET surface area of 313.325m^2/g and 285.021m^2/g for EFBZ and EFBP, respectively. The BET surface area of the activated carbons produced using phosphoric acid was lower than that produced using zinc chloride, which may be due to the presence of phosphates within the carbon as a result of the incorporation of phosphate and polyphosphate species structures through C-O-P bonds. Removing chemicals from the carbonized sample by washing yields porosity in the carbon matrix. As can be seen from the table, there is no significant difference in the ratio of micropore area to external surface area of the two activation agent [22].

Table 2: Surface area properties of the Char Co-pyrolysis

Sample	S_{BET} (m^2/g)	S_{mi}	S_{mi}/S_{BET}
100%EFB	251.00	249.03	0.992
10%LDPE 90%EFB	285.02	327.30	1.148
20%LDPE 80%EFB	593.27	595.60	1.004
30%LDPE 70%EFB	362.32	390.20	1.077
40%LDPE 60%EFB	325.38	383.20	1.177

The result in Table 2 presents the BET specific surface area analyses for EFB co-pyrolysis with the LDPE. The results indicated that co-pyrolysis has a strong synergistic effect on the char. It was perceived that 20% LDPE loading on the fiber showed surface area. The result shows that an increase in plastic loading increases the surface area and pore volume but reduces it when loading is increased to 40% LDPE. It was reported that bio-char from EFB palm oil has benefits not only for sequestering carbon for climate change and mitigation but also for improving soil health and crop performance [23]. Pyrolysis at lower temperatures would result in a large amount of char, but at a pyrolysis temperature of 500

°C, high porosity structures from the bio-char product are expected to be sufficiently developed during the pyrolysis process [24]. All the BET surface areas from the present study are significantly higher than those of Hadjar et al. [25] (21.9m^2/g and 24.2, respectively, using the same sample. It has been found that increasing pyrolysis temperature causes changes in bio-char surface area and porosity, which may be attributed to the decomposition of organic matter and the formation of microspores. Also, the destruction of aliphatic alkyls and ester groups as well as the exposure of the aromatic lignin core under higher pyrolysis temperatures may result in increased surface area. Biochar becomes thermally stable and more hydrophobic at temperatures above 650 °C [26].

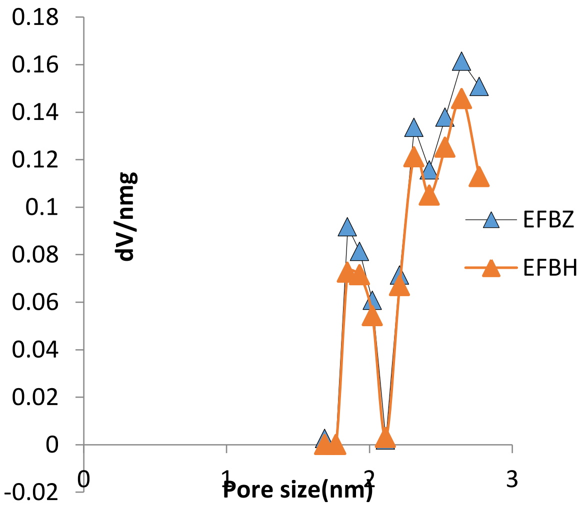

Figure 1: The pore size distribution of the activated carbon

The pore size distribution of the prepared ACs calculated using the DFT method is shown in figure 1. The distribution curve indicates that the pore width of all the AC is in the range of 1.6-2.7nm. The average pore size of the activated carbon materials was within the range of less than 2 and 2–50 nm, which indicates that the activated carbon produced has an appreciable number of micropores and mesopores according to the International Union of Pure and Applied Chemistry (IUPAC) classification. It is known that the microporosity of the activated carbon is a factor of the nature of the precursor and the activation conditions. The influences of chemical agents on the pore volume are shown in Fig. 2. The figure shows that the micropores were developed in the activated carbon. The pore volume created by zinc chloride activation is higher than that by phosphoric acid. This observation is in agreement with the results of [27].

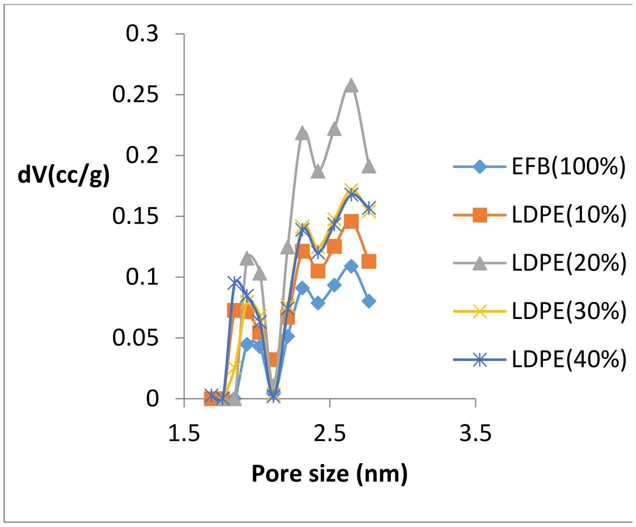

Figure 2: Pore size distribution of the co-pyrolysis product char

Adsorption capability of activated carbon is primarily determined by the volume and size of their nanopores, which are typically in the microporous range [28]. The surface area and porosity of the carbon directly relate to the physical and chemical properties of the raw materials, processing methods, and production conditions. Figure 1 demonstrates the adsorption isotherms of nitrogen at 77K of the char product obtained at the end of co-pyrolysis. Thus, all the samples displayed characteristics [29]. Similarly, the result of pore size distribution (PSD) presented in Figure 2 shows the pore distribution of the samples produced through the co-pyrolysis of EFB with LDPE, obtained using a DFT model. All the samples show broad peaks in the microporous condition region. Thus, the pore characteristics of the samples are within the micropore range (2 nm). Similarly, higher peaks are distributed across a broad mesoporous range (2 nm pore width 50 nm). Among the strongest peaks with a narrow PSD are 20%LDPE and 90%EFB fiber, which have a large surface area. Therefore, this serves as a good combination for the production of high surface area and pore volume activated carbon through pyrolysis. A cleaner surface of activated carbon may be attributed to the removal of impurities and volatile substances during activation.

CONCLUSIONS

The comparison between the Phosphoric acid and Zinc chloride activation agents was studied, where the results showed that the activated carbon prepared from Zinc Chloride has a higher surface area and pore volume than Phosphoric acid. The pore size distribution of the prepared ACs calculated using the DFT method indicate that Activated carbons are in the range of 1.2.-7nm, which reveals that the activated carbon produced has an appreciable number of micropores and mesopores. The surface area and porosity of the EFB fiber and LDPE of co-pyrolysis char product samples are in the microporous condition region. Therefore, the fiber can be attributed to produce high surface area and pore volume activated carbon through pyrolysis as well as through chemical activation.

Conflict of Interest

We are confidence that there is of no any conflicts of interest associated with this publication and there has been no financial support for this work that could have influenced its outcome. As Corresponding author, I confirm that the manuscript has been read and approved for submission by all the named author

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