Physical Activation of Oil Palm Empty Fruit Bunch via CO2 Activation Gas for CO2 Adsorption

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Abstract. In this study, different parameters for the preparation of activated carbon were investigated for their yield and CO2 capture capabilities. The activated carbon was prepared from Oil Palm Empty Fruit Bunch (OPEFB) via a 2-step physical activation process. The OPEFB was pyrolyzed under inert conditions at 500 °C and activated via CO2. A 2-factorial design was employed and the effects of activation temperature, activation dwell time and gas flow rate on yield and CO2 capture capabilities were compared and studied. The yield obtained ranged from between 20 – 26%, whereby the temperature was determined to be the most significant factor in influencing CO2 uptake. The CO2 capture capacity was determined using Temperature Programmed Desorption (TPD) technique. The CO2 uptake of EFB activated carbon achieved was between 1.85 – 2.09 mmol/g. TPD analysis has shown that the surface of AC were of basic nature. AC was found to be able to withhold the CO2 up to 663°C before maximum desorption occurs. The surface area and pore size of OPEFB obtained from BET analysis is 2.17 m2 g-1 and 0.01 cm3 g-1. After activation, both surface area and pore size increased with a maximum observed surface area and pore size of 548.07 m2 g-1 and 0.26 cm3 g-1. Surface morphology, functional groups, pore size and surface area were analyzed using SEM, FT-IR, TPD and BET.

1. Introduction

In recent years, researchers are concern about the environment due to global warming, which has resulted in the change in climate and weather patterns. This has in turn driven researchers to focus on developing improved and efficient methods and technologies to reduce the environmental impact from human activities. Many reports have shown that the global temperature has risen with measurable consistency to the increase in atmospheric CO2. In the mid 1960’s, the global temperature has risen by 0.2°C and by the 1980’s, the global temperature has again risen by 0.4°C [1]. This is further supported by a mathematical model done by Specht et al., 2016 and a continued increase in temperature is predicted in the near future [2].

Among the many contributors of global warming are the anthropogenic emissions of CO2 gases [3]. It has been reported that CO2 has the highest negative impact on the observed greenhouse effect, which causes up to approximately 55% of the global warming [4]. This is mainly attributed to CO2 causing greater adsorption of thermal radiation from the Earth’s surface and thus, increases the overall air temperature within the troposphere [5].
Many alternative solutions are being proposed to tackle this situation. Carbon Capture and Storage (CCS) technologies is currently the most viable short term option to reduce the anthropogenic CO₂ emissions from industrial sources (Metz et al., 2005; Yang et al., 2008). One of the promising technologies of CCS is to employ carbonaceous materials for the adsorption of CO₂. Carbonaceous materials which are converted to activated carbon (AC) has been proven to be exceptional in capturing post-combustion CO₂ [6]. Commercially, AC is one of the most common adsorbents used for the removal of organic compounds from both air and water sources. This is because the raw materials required to produce AC are cheap and abundant.

Production of activated carbons is carried out by pyrolysis from a precursor; mainly from an organic substance or synthetic polymers into char. The char produced from pyrolysis yields varying degree of surface area and porosity, which depends on the material used and also pyrolysis conditions. However, the surface area and porosity may be insufficient for industrial applications [7]. Therefore, further activation, either by physical or by chemical process, is required. Agricultural by-products have been widely used as the raw material due to its high carbon content, low inorganics and availability at low prices or sometimes freely available as it is considered as waste materials [8].

Oil palm is one of the most economical perennial oil crops for its valuable oil-producing fruits in tropical regions such as West Africa and Southeast Asia [9]. Malaysia is currently the world’s largest exporter of palm oil. Malaysia contributes to about 47% of the world’s supply of palm oil. Malaysia also accounts the highest percentage of global vegetable oils and fats trade in year 2005 [10]. Therefore, in this study, the agricultural waste, which is the oil palm empty fruit bunch (OPEFB), is studied for its suitability as a precursor to preparing AC for CO₂ capture.

2. Materials and Method

2.1. Materials
The OPEFB is collected from a local oil palm plantation, in Kota Kinabalu, Sabah, Malaysia. The OPEFB collected were thoroughly washed to remove unwanted impurities such as dirt, pesticide residue and other inorganic compounds. Then, it is thoroughly dried and cut into small pieces, approximately 2-3 cm and further washed with hot water to remove excess oil. These small pieces were placed in the oven overnight at 130 °C, for drying. The drying process will to reduce the moisture content in the empty fruit bunch. After that, the empty fruit bunches were grounded and sieved, using a mechanical sieve, to a size of 2-3 mm. Finally, it is stored in an air-tight container, for further analysis and processing.

Two-step physical activation was chosen to prepare AC from OPEFB. Carbonization of the raw OPEFB were carried out in a horizontal tube furnace (LT furnace model STF50-1200), at 500°C under N₂ flow for 2 hours. Then, for the activation process, N₂ was stopped and gasification by CO₂ was carried out at different activating temperatures, dwell time and CO₂ flowrate. The experimental parameters, the percentage of yield and resulting CO₂ uptake is shown in table 1.

2.2 Characterization
The constituents of OPEFB were determined using Thermogravimetric analysis (TGA). The sample was heated in an inert condition, from 30°C to 700°C at a ramping rate of 5°C per minute. Fourier Transform Infrared spectroscopy (FTIR) was used to characterize the surface functional groups of both the OPEFB and the prepared AC surface. Scanning electron microscopy (Hitachi S-3400 SEM) and energy dispersive X-ray spectrometry (EDX) were used to observe the morphology and to conduct the elemental mapping of the samples. The acid/base character of the surface groups of the carbon samples were determined by Temperature Programmed Desorption (ThermoFinnigan TPDRO 1100 Series).
2.3 CO₂ Adsorption
CO₂ adsorption capacity of the AC were determined by temperature-programmed desorption coupled with spectrometry (TPD–MS). Each AC sample weighing approximately 5 mg was placed in a quartz tube in a furnace. The AC was pretreated by flowing Nitrogen gas into the chamber before the analysis to produce an inert environment. Then, CO₂ gas was flowed into the chamber for an hour with simultaneous heating causing the AC pores to become saturated with CO₂. After that, Nitrogen gas was passed through for 5 minutes under low temperature to remove excess CO₂. Finally, Helium gas was flowed into the chamber with a linear heating rate of 5 °C/min in vacuum of up to 900°C. The mass spectrometer was set to detect CO₂. The total amount of CO₂ desorbed is the total uptake capacity of CO₂ by the AC.

3. Results and Discussion

Table 1. Activation conditions, percentage of yield and CO₂ uptake capacity

| Preparation parameters | CO₂ adsorption capacity (mmol/g) |
|------------------------|----------------------------------|
| AC Sample | Temp (°C) | Time (hr) | Flow (mL/min) | Yield (%) |
| 1 | 500 | 1 | 30 | 25.57 | 2.09 |
| 2 | 700 | 1 | 30 | 20.55 | 1.93 |
| 3 | 500 | 3 | 30 | 25.16 | 2.01 |
| 4 | 700 | 3 | 30 | 20.42 | 1.93 |
| 5 | 500 | 1 | 50 | 24.48 | 2.08 |
| 6 | 700 | 1 | 50 | 20.76 | 1.86 |
| 7 | 500 | 3 | 50 | 25.06 | 2.01 |
| 8 | 700 | 3 | 50 | 20.32 | 1.86 |

3.1. Characterization

3.1.1. Thermogravetric Analysis. OPEFB is a lignocellulosic biomass, which is mainly composed of cellulose, hemicellulose and lignin, as well as other minor components [11]. A study was made by Vamvuka et al., which shows the TG analysis of olive kernel and cotton residues. In this study, the main thermal decomposition of lignocellulosic materials was found to occur over the temperature range of 200 – 400°C. Lignin was the first component to decompose at a low temperature which continues on until approximately 900°C. Hemicellulose is a light fraction component which also decomposes at the low temperature regions, ranging from 160 and 360°C. Lastly, cellulose was determined to be the last component to decompose at the high temperatures, ranging from 240 – 390°C [12].

The thermogravimetric (TG) data and its first derivative (DTG) data of oil palm OPEFB were plotted. The OPEFB sample was pyrolyzed at 5°C/min from 50°C to 700°C. From the graph in figure 1 it can be seen that pyrolysis of oil palm EFB starts above 250°C. From the DTG curve, the maximum rate of decomposition was observed at approximately 300° C, with a smaller shoulder on the lower temperature side.

This indicates that there is at least one major reaction scheme occurring during the pyrolysis process. The maximum peak observed on the DTG curve is probably contributed by the decomposition of the lighter fraction (i.e. cellulose) and the small shoulder corresponds to the decomposition of the heavier component (i.e. hemicellulose).

The graph and result obtained is similar to the results obtained by Luangkiattikhun et al., who studied the thermal decomposition of palm shell, fibre and kernel [13], and Vamvuka et al., who studied the thermal decomposition of olive kernel and cotton residues [12].
3.1.2. Fourier Transformed Infrared. The FTIR spectra of the raw OPEFB and AC were presented in figure 2. Each peak found in the OPEFB were labeled and assigned accordingly in table 2. Based on the figure, a broad adsorption peak for raw OPEFB is observed at 3345 cm⁻¹ which is attributed to O-H stretching functional group and this indicates the presence of bonded hydroxide in the raw EFB. The EFB sample also shows two other prominent adsorption peaks at 1252 cm⁻¹ and 1041 cm⁻¹ which refers to C-O stretching functional group.

For activated carbon OPEFB, during the carbonization and activation process most of the adsorption peaks of functional groups have disappeared. This is because the functional groups from the raw material spectrum were vaporized as volatile materials when heat was supplied to the sample [14]. This shows that the activation process has taken place successfully.
Figure 2. FTIR spectra of Raw EFB and AC EFB

Table 2. FTIR peaks and its corresponding assignments

| Wave number (cm⁻¹) | Assignments                                           | EFB | AC |
|--------------------|-------------------------------------------------------|-----|----|
| 3500 – 3200        | O-H Stretching                                        | ✓   |    |
| 2930 – 2900        | C-H Asym. Stretching                                  | ✓   |    |
| 1610 – 1640        | C=C Aromatic skeletal stretching                      | ✓   |    |
| 1240 – 1280        | C-O Asym. stretching of aromatic ethers, esters and phenols | ✓   |    |
| 1260 – 1000        | C-O Carboxylic acids, alcohols, phenols and esters or the P=O bond in phosphate esters | ✓   |    |
| 700 – 400          | C-C stretching                                        | ✓   | ✓  |
3.1.3. Temperature Programmed Desorption. Temperature programmed desorption (TPD-CO$_2$) analysis was carried out on selected AC samples, prepared at pyrolysis temperature 500°C and 700°C. From figure 3, the TPD-CO$_2$ profile shows the basic sites density and basic strength of the AC and AC-ZIF. Both AC shows two desorption peaks. The desorption peaks at $T_{\text{max}}$ 269°C and 445°C can be assigned to weak and medium basic sites whereas $T_{\text{max}}$ > 600°C can be assigned to super basic sites. These basic sites can be attributed with the resonating $\pi$-electrons of the carbon aromatic rings which attract protons and also the basic surface functional groups such as nitrogen containing groups [15]. These basic sites may also be caused by the high pyrolysis temperature used. Studies have shown that a there is a decomposition of oxygen functional groups at elevated temperatures, which in turn increases the basicity of carbon surface [16]. It was also stated in a research by Shafeeyan and his team of researchers than carbon with a more basic surface area is more favorable for CO$_2$ capture [15].

![Figure 3. TPD-CO$_2$ Profile for AC and AC-ZIF](image)

3.1.4. Scanning Electron Microscopy (SEM). The SEM images of the activated carbons are shown in figure 4. Figure 4(a) and 4(b) shows the SEM images of OPEFB before activation, whereas 4(c) and 4(d) shows the OPEFB after activation. By comparing figure 4(a) and 4(c), the pyrolyzed OPEFB showed a much denser ridges and rougher surface compared to the raw OPEFB. This roughness is increased during the CO$_2$ activation which resulted in largely uniformed pores. The comparison of pore can be seen in figure 4(b) and 4(c).
3.2. Yield of AC prepared using different parameters

Table 1 summarizes the parameters of pyrolysis or activation used in this experiment and also the yield of each set of parameters and is represented in a 3d plot in figure 5. From the figure, it can be seen that the most prominent parameter affecting the yield is the activation temperature. As temperature increases, yield decreases. This is primarily due to the moisture evaporation and also large amount of volatiles released during the pyrolysis stage. The large amount of volatiles released, known as the devolatilisation step, can be mainly attributed to the decomposition of cellulose, hemicelluloses and lignin found in the OPEFB [17]. The duration of dwell time shows very little effect on the yield, whereby a longer dwell time decreases the yield of activated carbon. This is also attributed to devolatilisation, as a longer dwell time allows for higher loss of volatile matter [18]. The different flow rate of CO₂ however, shows no identifiable trend and effects towards the yield of activated carbon.

Figure 4. SEM images of Activated carbon
3.3. \( \text{CO}_2 \) uptake capacity

From the table 1 and figure 6, it can be seen that the adsorption capacity of \( \text{CO}_2 \) decreases when using AC prepared at higher activating temperature and longer dwell time. The highest amount of \( \text{CO}_2 \) adsorbed was 2090 \( \mu \text{mol/g} \), achieved by the AC produced at activating temperature of 500 °C and 1 hr dwell time. A higher activating temperature and longer dwell time may increase surface functional group which contains oxygen. This may lead to acidic oxidation which in turn leads to pore blocking [17].

![Figure 5. 3D plot of Activation Parameters against Yield](image)

![Figure 6. 3D plot of Activation Parameters against CO\(_2\) uptake capacity](image)
3.4. BET Analysis

Table 3. BET analysis of selected samples

| Sample    | BET surface area (m² g⁻¹) | total pore volume (cm³ g⁻¹) |
|-----------|---------------------------|----------------------------|
| Raw EFB   | 2.17                      | 0.0100                     |
| AC 700    | 14.32                     | 0.0123                     |
| AC 500    | 548.07                    | 0.2552                     |

![N2 isotherms](image)

Figure 7. N₂ isotherms of (a) OPEFB, (b) EFB-AC activated at 700 °C and (c) EFB-AC activated at 500 °C

From the BET surface shown in table 3, higher surface area is seen after activation. All the samples after activation have shown an increase in surface area. AC prepared at 500 °C yields higher surface area than AC prepared at 700 °C. This is consistent with the uptake capacity of CO₂ shown in table 1. Figure shows graph of volume (Va/cm³ (STP) g⁻¹) against relative pressure (P/P₀) for OPEFB, AC activated at 700 °C and AC activated at 500 °C respectively. From figure 7(a), OPEFB shows type III isotherm [20], whereas figure 7(b) EFB-AC activated at 500 °C shows type I isotherm, which is assigned to microporous materials [21]. EFB-AC activated at 700 °C (figure 7(c)) however, shows a type IV isotherm with H₂ hysteresis loop. A review by Sing & Williams, 2004, relates the H₂ hysteresis loop with ink bottle pore system and also pore blocking effects [22]. Nguyen et al., 2013 came to the same conclusion whereby H₂ hysteresis loop represents either a cavitation or pore-blocking mechanism. Nguyen and his team further explain that this is caused when the cavity is stretched beyond its tensile strength [23]. This result in a lower adsorption capacity and pore size of the EFB-AC activated higher temperatures.
4. Conclusions

Porous activated carbon with high specific surface area, large pore volume, and wide pore-size distribution has been successfully produced from oil palm empty fruit bunch via 2 step CO\textsubscript{2} physical activation. The prepared carbon has shown to be able to adsorb and retain CO\textsubscript{2}. While its CO\textsubscript{2} capture abilities are still limited, the OPEFB has shown to be a promising adsorbent for CCS technology. Due to its abundance, it also provides a waste to wealth opportunity.

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