Comparison on pore development of activated carbon produced by chemical and physical activation from palm empty fruit bunch

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Abstract. It is well-known that activated carbon is considered to be the general adsorbent due to the large range of applications. Numerous works are being continuously published concerning its use as adsorbent for: treatment of potable water; purification of air; retention of toxins by respirators; removal of organic and inorganic pollutants from flue gases and industrial waste gases and water; recuperation of solvents and hydrocarbons volatilized from petroleum derivatives; catalysis; separation of gas mixtures (molecular sieve activated carbons); storage of natural gas and hydrogen; energy storage in supercapacitors; recovery of gold, silver and other noble metals; etc. This work presents producing activated carbons from palm empty fruit bunch using both physical activation with CO\(_2\) and chemical activation with KOH. The resultant activated carbons were characterized by measuring their porosities and pore size distributions. A comparison of the textural characteristics and surface chemistry of the activated carbon from palm empty fruit bunch by the CO\(_2\) and the KOH activation leads to the following findings: An activated carbon by the CO\(_2\) activation under the optimum conditions has a BET surface area of 717 m\(^2\)/g, while that by the KOH activation has a BET surface area of 613 m\(^2\)/g. The CO\(_2\) activation generated a highly microporous carbon (92%) with a Type-I isotherm, while the KOH activation generated a mesoporous one (70%) with a type-IV isotherm, the pore volumes are 0.2135 and 0.7426 cm\(^3\).g\(^{-1}\) respectively. The average pore size of the activated carbons is 2.72 and 2.56 nm for KOH activation and CO\(_2\) activation, respectively. The FT-IR spectra indicated significant variation in the surface functional groups are quite different for the KOH activated and CO\(_2\) activated carbons.

1. Introduction
Activated carbons are the most versatile and commonly used adsorbents because of their extremely high surface areas and micropore volumes [1], large adsorption capacities, fast adsorption kinetics, and relative ease of regeneration [2]. They are produced from a variety of carbonaceous source materials. The choice of precursor is largely dependent on its availability, cost, and purity, but the manufacturing process and intended application of the product are also important considerations [4].

Precursors used for the production of activated carbons are organic materials that are rich in carbon, such as coal, lignite, and wood. Although coal is the most commonly used precursor, agricultural waste in certain condition is a better choice [1]. Activated charcoal produced from residues would reduce the pressure on forests since wood is also commonly used for this purpose [5]. Many agricultural by-products such as coconut shell [2,5,6], grain sorghum [7], coffee bean husks [8], rubber wood sawdust [9], chestnut wood [10], and fruit stones [11], have been discovered to be suitable precursors for activated carbon due to their high carbon and low ash contents. Agricultural wastes are considered to be a very important feedstock because of especially two facts: they are renewable sources and low cost materials [4].

Empty fruit bunches (EFBs) are major waste products generated from the palm oil industry. Every year, 25.9 and 19.8 million tons of oil palm EFB are produced in Indonesia and Malaysia, respectively [12]. EFB, which consists of high cellulose and hemicellulose contents and is available as a low-cost...
material, has gained attention as biomass feedstock for producing activated carbon [14,15]. Conversion of EFB to value-added product such as activated carbon would directly solve part of the environmental problems while utilizing abundant and low cost biomass.

The preparation of activated carbons consists of two main steps: carbonization of a carbonaceous raw material and char activation [16]. Activation can be done using gases such as carbon dioxide, steam, and others (physical activation) or dehydrating agents and oxidants, such as H₃PO₄, H₂SO₄, HNO₃, NaOH, KOH, and ZnCl₂ (chemical activation). Chemical activation is largely employed in the preparation of activated carbons. Among its advantages over physical activation processes are: (i) lower activation temperatures, between 600 and 800°C, as compared to the activation temperature between 700 and 1100°C used in physical activation [17], (ii) shorter activation times [19], (iii) single activation step (carbonization activation simultaneously), (iv) higher yields, and (v) better surface area. Basta et al. (2009) have reported that two-step KOH activation was more efficient in producing activated carbons than one-step KOH activation, as it gave better carbon yields [18]. In this process, KOH reacts with char, not with biomass, producing carbons with high surface areas. In contrast, some disadvantages are: (i) need for intense washing to remove process generated impurities (Na₂CO₃ and others), and (ii) general process corrosiveness [20].

The most important characteristic of an activated carbon is its adsorption performance which is highly influenced by the preparation conditions, as the activated carbon preparation variables will influence the pore development and surface characteristics of the activated carbon produced. The aim of this study is to prepare an activated carbon from palm empty fruit bunch (PEFB) that are abundant Indonesia by-products by using the physical activation with carbon dioxide (CO₂). The effect of activation temperature and time were investigated. The resultant activated carbons were characterized by several techniques.

2. Experimental

2.1. Apparatus

The schematic diagram of the experimental setup is shown in Figure 1.
2.2. Preparation of porous carbon by KOH activation

Palm empty fruit bunch (PEFB) was obtained from Oil Palm plantation on the Riau province in Indonesia. Two parts of PEFB of shaggy and core were prepared for the activated carbon precursors. PEFB was dried in an oven at 110°C for 6 h. It was then ground and sieved to a 20 or 30 mesh particle size prior to activation. PEFB with a particle size of 30 mesh was used for characterization and the production of activated carbons.

The dried PEFB was placed in a muffle furnace maintained at 400°C for 2 h. The carbon thus obtained was kept at 400°C in the muffle furnace and simultaneously purged with N₂ for 2 h. Then the temperature was reduced to room temperature to get the char. Finally the black residue was sieved to get PEFB having average particle size of 0.096 mm and was stored in air tight plastic container.

For chemical activation, the char was impregnated with a solution of the potassium hydroxide (KOH). Then the mixture was stirred at 80°C for 2 h in a stainless steel beaker. The temperature of the solution was later increased to the boiling point until complete dryness, which forced the incorporation of all chemical into the particles; at this stage, the temperature reached about 150°C. After being dried, the carbons were placed in sealed ceramic oven and heated at a rate of 10 °C/min to 800 °C. In the meantime, N₂ gas in a tubewas let into the oven by a rate of 200cm³/min. The time for activation at 800 °C was 1 h. The activated products were cooled to room temperature and washed with deionized water. The carbonized samples were repeatedly washed with water. Subsequent to this, a 5 M solution of HCl was used to remove the activating agent, followed by distilled water rinsings until free of chloride ions. The presence of chloride ions was verified by silver nitrate solution. Consequently, the samples were dried at 110 °C for 12 h.

2.3. Preparation of porous carbon by CO₂ activation

The dry PEFB sample (10 g) was loaded into a tubular furnace under N₂ flow (120 mL/min) and heated up to a carbonization temperature of 800 °C at a heating rate of 20 °C/min. The sample was held at 800 °C for 1 h. Then N₂ flow was switched to CO₂ flow with a rate of 50 mL/min for 2 hours for activation and finally CO₂ flow was switched back to N₂ flow and cooled down to room temperature under N₂ flow.

2.4. Characterization

The physico-chemical characteristics of activated carbon produced in this experiment were determined. Adsorption characteristics of the activated carbon samples were determined by nitrogen adsorption. The specific surface areas were determined from the isotherms using the Brunauer–Emmett–Teller equation. The surface functional groups were analyzed by using a FT-IR spectroscopy. The analysis of surface functional groups was based on the Boehm titration method. The basic groups were neutralized with 0.1 mol/L HCl solution, and the acidic groups were neutralized with 0.1 mol/L NaOH, Na₂CO₃ and NaHCO₃ solutions. The various free acidic groups were determined with the assumption that NaOH neutralizes carboxyl, lactone and phenolic groups, Na₂CO₃ neutralizes carboxyl and lactone groups and NaHCO₃ neutralizes carboxyl groups.

3. Results and Discussion

3.1. Textural characterization

Figure 2 shows the Nitrogen adsorption isotherms of activated carbons from PEFB produced at different activation method. The different shape of the adsorption isotherm is an indication of the different pore size distribution of the samples. It can be seen that the volume of nitrogen adsorbed increases by physical activation. By physical activation, the Nitrogen adsorption isotherm shows intermediate between types I and II of the referred IUPAC classification. Type I isotherms are given by predominantly microporous adsorbents having a relatively small external surface area. The adsorption capacity at relatively low relative pressures (P/Po) is very high, which indicates the presence of a well-developed microporous structure. Hysteresis is detected between adsorption and
desorption isotherms, indicating the presence of a little proportion of mesopores and macropores. The isotherms of chars prepared by chemical activation belong to type II IUPAC classification. As shown in Figure 2, the initial part of the type II isotherm for the chars represents micropore filling, and the slope of the plateau at high relative pressure is due to multilayer adsorption on the nonmicroporous surface, i.e., in mesopores, in macropores and on the external surface. The desorption isotherms presents a hysteresis loop at high relative pressure. The desorption isotherms is useful for determination of the mesoporous nature of activated carbons, and the presence of a hysteresis between the adsorption and desorption curves implies the existence of mesopore pores.

In accordance to the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC), adsorbent pores are classified into three groups: micropores (size <2 nm), mesopores (2–50 nm), and macropores (>50 nm). Micropores can be divided into ultramicropores (width less than 0.7 nm) and supermicropores (width from 0.7 to 2 nm). The size of pores that are formed would have an effect on the porosity, the total surface area that is available for adsorption and most importantly, the size of molecules that can diffuse into the solid. Thus the development of an appropriate pore structure is necessary if the activated carbon produced is to be used for a particular application.

The effect of activation method on porosity development of activated carbon is shown in Table 1. The higher BET surface area is an indication of the existence of a significant amount of microporosity. By physical activation, the adsorption capacity of the activated carbon increased enhancing the amount of microporosity. A more ordered structure is likely to be developed in the char that leads to a slower rate of gasification in the interior of the particle. From Table 1, it was observed that the BET surface area, total volume and micropore volume of activated carbon prepared increased, while average diameter decreased. The highest the BET surface area, total volume and micropore volume were obtained by using physical activation.

**Table 1.** Characteristics of porosity in PEFB activated carbons prepared different activation method.

| Parameter     | Chemical Activation | Physical Activation |
|---------------|---------------------|---------------------|
| $S_{BET}$ (m$^2$/g) | 405.81              | 661.46              |
| $V_{tot}$ (cm$^3$/g)  | 0.1590              | 0.2455              |
| $V_{micro}$ (cm$^3$/g) | 0.1177              | 0.1989              |
| $D_{avg}$ (nm)     | 3.63                | 2.48                |

**Figure 2.** Adsorption/desorption isotherms of N$_2$ at 77 K for PEFB activated carbons prepared different activation method.
Figure 3 illustrated the pore size distributions of activated carbons prepared at different activation method. Pore-size distribution is the principal factor determining the adsorption characteristics of activated carbons. The structural heterogeneity of porous materials is generally characterized in terms of the pore size distribution. The pore size distribution represents a model of solid internal structure and regularly shaped model pores which represent the complex void spaces within the real solid. This figure confirmed that the activated carbons prepared by physical activation had more microporous structures compared to activated carbons prepared by chemical activation.

3.2. Chemical surface characterization

Table 2 shows the elemental analyses of PEFB activated carbon produced at activation method. Results indicate the presence of many elements with predominance of carbon in both of the samples. The percentage of carbon increased after activation. These increases in carbon percentage are essentially due to the loss of volatile matter and the decomposition of cellulose and hemicellulose during pyrolysis, and, on the other hand, to the decomposition of lignin during activation. Table 2 also shows a decrease in the H/C and O/C ratios when using physical activation. Physical activation may cause more heteroatoms to evaporate from the carbon rings and an increasing number of C-H bonds are ruptured as the activation of the char support progresses.

Table 2. Elemental analysis of the PEFB activated carbons produced at different activation method.

| Elemental (wt %) | Chemical Activation | Physical Activation |
|-----------------|---------------------|---------------------|
| C               | 69.19               | 81.38               |
| H               | 0.41                | 0.39                |
| O               | 15.96               | 6.04                |
| H/C             | 0.0059              | 0.0048              |
| O/C             | 0.2307              | 0.0742              |
The oxygen functional groups are very important characteristics of the activated carbons because they determine the surface properties of the carbons and hence their quality as ion exchangers, adsorbents, catalysts, and catalyst supports. The contents of oxygen-containing functional groups with various acidity strength (total acidic groups: carboxyl, lactonic, hydroxyl and carbonyl) as well as, the total amount of the basic groups are presented in Table 3. It shown in Table 3, for activated carbons prepared by chemical activation, the total oxygen functional groups is 0.196 mmol.g⁻¹ with a breakdown of 0.196 mmol.g⁻¹, 0.196 mmol.g⁻¹, and 0.196 mmol.g⁻¹, individually, for carboxylic, lactone and phenolic groups. When the activated carbons prepared by physical activation, the total oxygen containing functional group decreases to 0.240. Decrease in oxygen containing functional groups, takes mostly in the carboxylic, lactone and phenolic groups. The phenolic group decreases to 0.240. Meanwhile the lactone group decreases to 0.240. While the concentration of the carboxylic groups decrease to 0.240.

| Activation method  | Carboxylic (mmol.g⁻¹) | Lactonic (mmol.g⁻¹) | Phenolic (mmol.g⁻¹) | Basic (mmol.g⁻¹) | pH_{pzc} |
|-------------------|-----------------------|---------------------|---------------------|-----------------|---------|
| Chemical Activation | 0.664                 | 0.012               | 1.143               | 1.635           | 5.36    |
| Physical Activation | 0.427                 | 0.011               | 0.745               | 0.867           | 5.86    |

The FTIR spectroscopy provides information on the chemical structure and functional group of PEFB and its chars prepared at different activation method, shown in Figure 4. Typical infrared band assignments for PEFB indicate that, PEFB contains a number of atomic groups and structures. The functional groups O–H, aromatic C=C, aliphatic C–H, olefinic C=C, C–O, C–O–C, C=O, CH₃, C–O–H and Si–O–Si bands are contained in the PEFB. The band at 3415 cm⁻¹ O–H is corresponding to (O–H) vibrations in hydroxyl groups. The position and shape of this band suggest that the hydroxyl groups are involved in hydrogen bonding. Water residual in PEFB could take part in the formation of hydrogen bonds. According to the four types of hydrogen-bonded structures, the pre dominant one in PEFB is self-associated OH groups. The fact that the band at 3415 cm⁻¹ is somewhat broader towards lower wavenumbers suggests that PEFB also contains OH-ether hydrogen bonds. The band at 2919 cm⁻¹ representing the presence of (C–H) vibrations. The appearance of (C–H) adsorption bands indicating the presence of methyl and methylene groups in PEFB. However, the peak at 1459 cm⁻¹ was attributed to (CH₃) stretching vibration. The characteristic absorption of methyl group at 1375 cm⁻¹ is valuable for methyl group estimation. Hence the band at 1459 cm⁻¹ is slightly weaker than the band at 1375 cm⁻¹, proving the presence of acetoxyl groups (–O–COCH₃) in PEFB. The band at 1732 cm⁻¹ indicating the presence of (C=O) vibrations in carbonyl groups, shows the presence of acetyl derivative groups, aldehydes groups, and others. The olefinic (C=C) and aromatic (C=C) vibrations were detected at 1635 cm⁻¹ and (1606–1459 cm⁻¹) region, respectively. While, alkyl groups were detected from the C–CH₃ blending vibration at 1326 cm⁻¹. Moreover, the bands between 1100 and 1300 cm⁻¹, the (C–O–H) vibrations in phenolic and (C–O–C) vibrations can be related to asymmetric vibrations in single graphitic sheet and between two such sheets; oxygen can act as a crosslinking agent between aromatic sheets. The absorbance band at 1000–1100 cm⁻¹ are attributed to (C–O) vibrations in primary C–OH, secondary O–H and the presence of silica, Si–O–Si. Furthermore, some bands are observed in the region 470–900 cm⁻¹, which are band positions compatible with C–H vibrations in olefinic or aromatic structures.
**Figure 4.** The FT-IR spectra of the PEFB activated carbons produced at different activation method.

| Material                        | Activation condition | $S_BET$ (m²/g) | $V_{mic}$ (cm³/g) | $V_t$ (cm³/g) | Pore size (nm) | References                  |
|---------------------------------|----------------------|----------------|-------------------|---------------|----------------|-----------------------------|
| Palm empty fruit bunches        | KOH                  | 488.51         | 0.2539            | 0.196         | 2.079          | Arshad et al.               |
| Peanut hull                     | Steam, 600 °C/2 h    | 253            | 0.09              | 0.22          | –              | Girgis et al.               |
| Coconut shell                   | CO₂, 600 °C/2 h      | 1700           | 0.88              | 1.14          | 2.7            | Guo et al.                  |
| Coconut shell                   | Steam, 1000 °C/120 min | 1926         | 0.93              | 1.26          | 2.6            | Li et al.                   |
| Sugarcane bagasse               | CO₂, 850 °C/2 h      | 625.6          | 0.097             | 0.040         | 1.454          | Goncalves                   |
| Peanut hull                     | Steam, 600 °C/2 h    | 253            | 0.09              | 0.22          | –              | Girgis et al.               |
| Coconut shell                   | CO₂, 600 °C/2 h      | 1700           | 0.88              | 1.14          | 2.7            | Guo et al.                  |
| Palm shell                      | ZnCl₂                | 1118           | 0.42              | 0.51          | 2.24           | Arami-Niya                  |
| Palm shell                      | CO₂, 800 °C/4 h      | 544            | 0.26              | 0.27          | 1.95           | Arami-Niya                  |
| Bagasse                         | ZnCl₂                | 923            | –                 | 0.53          | 0.8            | Boonpook et al.             |
| Rice husk                       | ZnCl₂                | 927            | –                 | 0.56          | 0.8            | Boonpook et al.             |
| Palm empty fruit bunches        | CO₂, 800 °C/2 h      | 717            | –                 | 0.7426        | 2.56           | This paper                  |
| Palm empty fruit bunches        | KOH                  | 613            | –                 | 0.2135        | 2.72           | This paper                  |
4. Conclusions
A comparison of the textural characteristics and surface chemistry of the activated carbon from palm empty fruit bunch by the CO$_2$ and the KOH activation leads to the following findings: An activated carbon by the CO$_2$ activation under the optimum conditions has a BET surface area of 717 m$^2$/g, while that by the KOH activation has a BET surface area of 613 m$^2$/g. The CO$_2$ activation generated a highly microporous carbon (92%) with a Type-I isotherm, while the KOH activation generated a mesoporous one (70%) with a type-IV isotherm, the pore volumes are 0.2135 and 0.7426 cm$^3$.g$^{-1}$ respectively. The average pore size of the activated carbons is 2.72 and 2.56 nm for KOH activation and CO$_2$ activation, respectively. The FT-IR spectra indicated significant variation in the surface functional groups are quite different for the KOH activated and CO$_2$ activated carbons.

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References
[1] Do D D 1998 Adsorption Analysis: Equilibria and Kinetics, Imperial College Press, London
[2] Hu Z., Srinivasan M P 1999 Microporous Mesoporous Mater 27 11-18
[3] Hidayat A, Rochmadi, Wijaya K, Hinode H, Budiman A 2013 Asian J Chem 25(3) 1569-1579
[4] Stavropoulos G G, Zabaniotou A A 2005 Microporous Mesoporous Mater 83 79–85
[5] Mozammel H M, Masahiro O, Bhattacharya S C 2002 Biomass Bioenergy 22 397–400
[6] Sekar M, Sakdi V, Rengaraj S 2004 J Colloid Interface Sci 279 307–313
[7] Diao Y, Walawender W P, Fan L T 2002 Bioresour Technol 81 45–52
[8] Baquero M C, Giraldo L, Moreno J C, Suarez-Garcia F, Martinez-Alonso A, Tascon J M D 2003 J. Anal. Appl. Pyrol. 70 779–784
[9] Srinivasakannan C, Bakar M Z A 2004 Biomass Bioenerg. 27 89–96
[10] Gomez-Serrano V, Cuerda-Correa E M, Fernandez-Gonzales M C, Alexandre-Franco M F, Macias-Garcia A 2005 Mater. Lett. 59 846-853
[11] Puziy A M, Poddubnaya O I, Martinez-Alonso A, Suarez-Garcia F, Tascon J M D 2005 Carbon 43 2857–2868
[12] Bardant T B, Sudiyarmanto S, Abimanyu H, Hanum A K 2013 Indones. J. Chem. 13 (1) 53-58
[13] Daud W R W and Law K N 2011 Bioresources 6 (1) 901-917
[14] Misson M, Haron R, Kamaroddi M F A, Amin N A S 2009 Bioresource. Technol. 100 2867-2873
[15] Parshetti G K, Hoekman S K and Balasubramanian R 2013 Bioresource. Technol. 135 683-689
[16] Ioannidou O, Zabaniotou A 2006 Renew. Sust. Energ. Rev. 11 1966-2005
[17] El-Hendawy A A, Alexander A J, Andrews R J, Forrest G 2008 J. Anal. Appl. Pyrol 82 272-278
[18] Basta A H, Fierro V, El-Saied H, Celzard A 2009 Bioresour. Technol. 100 3941-3947
[19] Nowicki P, Pietrzak R, Wachowska H 2008 Fuel 87 2037-2040
[20] Lozano-Castello D, Calo J M, Cazorla-Amoros D, Linares-Solano A 2007 Carbon 45 2529-2536
[21] Girgis B S, Yunis S S, Soliman A M 2002 Mater. Lett. 57 164–172
[22] Guo S, Peng J, Li W, Yang K, Zhang L, Zhang S, Xia H 2009 Appl. Surf. Sci. 255 8443–8449
[23] Boonpook A, Chiarakorn S, Laosiripojana N, Towprayoon S, Chidthaisong A 2011 J. Sustain. Energ. Environ. 2 77–81
[24] Li W, Yang K, Peng J, Zhang L, Guo S, Xia H 2008 Ind. Crops. Prod. 28 90–198
[25] Niya A A, Daud W M A W, Mjalli F S 2011 Chem. Eng. Res. Des. 8(9) 657–664
[26] Goncalves G C, Pereira N C, Veit M T 2016 Biomass Bioenerg. 85 178-186
[27] Arshad S H M, Ngadi N, Aziz A A, Amin N S, Jusoh M, Wong S 2016 J. Energy Storage Available online 8 October 2016