

Preparation and Characterization of Activated Carbon from the Pyrolysis of Physic Nut (*Jatropha curcas* L.) Waste[†]

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Use of waste as raw material for producing porous carbon was investigated in this work. Physic nut (*Jatropha curcas* L.) residue from oil extraction for biodiesel production was pyrolyzed at 400–800 °C with hold times of 15, 120, and 240 min to obtain char precursors. Activated carbon, with favorable Brunauer–Emmett–Teller surface area in a narrow range, was prepared by soaking these chars in concentrated KOH, H₃PO₄, as well as a pure CO₂ gas flash activator. The maximum specific surface area of 532.30 m² g^{−1} was developed for the alkaline-treated sample. The carbon fraction of activated materials was as much as 90 wt %, significantly higher than the char precursor. Mesopore of 2–50 nm and total pore volumes of the materials were also significantly enhanced by these activations. Nitrogen adsorption isotherms of physic-nut-waste-activated carbons indicated that they were mainly mesopores. Pores of char activated by KOH and H₃PO₄ are irregular, of different shapes and sizes, and the macropores seemed to be connected to mesopores, especially for the KOH-activated case. Surface analysis of pyrolyzed and activated char using Fourier transform infrared spectroscopy indicated main functional groups that are considerably different to those of activated materials, which may lead to greater adsorption potential of activated samples. However, functional groups on each activated carbon are quite similar even with different activation processes. According to the data obtained, physic nut residue pyrolyzed at 800 °C and followed by KOH activation could be used as a low-cost adsorbent with favorable surface properties.

1. Introduction

Surging fossil fuel costs along with adverse environmental impacts from their usage leads to expanded production and use of bioenergy. One of the promising plant resources for oil is physic nut (*Jatropha curcas* L.). Oil from its seed may directly fuel slow-speed diesel engines. Upgrading this oil by transesterification makes it a suitable replacement of conventional diesel. However, extraction of bio-oil from physic nut results in agricultural waste. Land fill, fertilization, incineration, and animal feed have been applied to manage this waste, with several logistical problems. A more viable option would be on-site conversion of this waste into value-added product, such as activated carbon, which can be used locally or sold as a raw material for many industries.

Activated carbon, also known as porous carbon, has been widely used as an adsorbent in the separation and purification of gas or liquid. The application of these carbons has been considered a major unit operation in the chemical and petrochemical industries.^{1,2} In addition to serving as an adsorbent,

high porosity carbons have recently been applied in the manufacture of high-performance layer capacitors. Because of the introduction of rigorous environmental regulations and the development of new applications, the demand for porous carbons is expected to increase progressively.³

Typically, the preparation of activated carbon can be divided into two processes. First, the physical method consists of the pyrolysis of the precursor material and gasification of the resulting char in steam or carbon dioxide. The formation of the porous structure is achieved by elimination of a large amount of internal carbon mass. High porosity carbons can be obtained only at a high degree of char burn off. For the chemical method, pyrolysis char would be impregnated with some chemical reagents, such as ZnCl₂, H₃PO₄, NaOH, and KOH. Because of the dehydrogenation process, the chemical reagents promote the formation of cross-links, leading to the development of a rigid matrix, less prone to volatile loss and volume contraction upon usage.^{4–7} Major advantages of the chemical activation compared to the physical activation are lower treatment temperatures and shorter treatment times. In addition, activated carbon obtained

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Table 1. Chemical Characteristics of Physic Nut Waste Used as Raw Material for Pyrolysis

proximate analysis (wt %)		ultimate analysis ^a (wt %)		composition (wt %)	
volatile	55.40	carbon	45.50	hemicellulose	17.47
fixed carbon	37.20	hydrogen	7.20	cellulose	56.31
ash	6.30	nitrogen	4.00	lignin	23.91
moisture	0.68	oxygen ^b	43.30		

^a Moisture and ash free. ^b By difference.

by chemical activation exhibits a larger surface area and better developed mesoporosity than physical activation.

Preparation of activated carbon using chemical and physical activation has been widely studied using various low-cost biomass materials, such as coconut shell, nut shell, and apple pulp, to name a few.^{8–10} However, there has been no report on activated carbon prepared from physic nut waste. Thus, how the difference in the method of activation affects the surface morphology of carbons derived from physic nut char could merit a thorough investigation. In the present study, the weight-loss behavior during pyrolysis of this waste material at high temperature, short hold time, and various particle sizes was studied to identify the optimum char production condition. The produced char was then used as the precursor and subjected to different activation agents, including KOH and H₃PO₄, along with physical activation by CO₂ to investigate the evolution of the surface characteristic and pore structure of these samples.

2. Experimental Section

2.1. Biomass Raw Material. Physic nut waste used in this study was obtained from an oil-extraction process using a twin screw extruder and sieved to the particle size of 0.43–0.50, 0.50–0.85, and 0.85–1.80 mm, respectively. The average proximate and elemental analyses of this material are shown in Table 1. This waste may be considered as a good candidate for conversion to activated carbon because of its relatively high carbon content and low ash, although its large portion of volatiles suggests that the substantial formation of liquid products through the pyrolysis process could be expected.

2.2. Thermogravimetric Analysis. Thermal degradation characteristics of physic nut waste were studied using a thermogravimetric method. Experiments were performed on a Mettler Toledo TGA/STDA851^e analyzer. Each sample of 5–6 mg was heated from room temperature to a final temperature of 900 °C at a heating rate of 15 °C/min under nitrogen atmosphere.

2.3. Pyrolysis Process. A vertical fixed-bed reactor was used as a pyrolyzer for char formation. The experimental setup is shown in Figure 1. The reactor is made of a 12 mm quartz tube with the height of 300 mm and a quartz frit as a retainer at a bottom end. The reactor is heated by a tubular ceramic furnace equipped with a photoionization detector (PID) temperature control and type K thermocouple placed at the center. In each run, approximately 3 g of sample material was placed on the top of the retainer and the system was then purged with 100 mL/min of N₂ for 15 min to ensure inert conditions in the bed. The reactor was then heated at a rate of 20 °C/min to a final temperature of 400–800 °C, while the physic nut waste was thermally decomposed to porous carbonaceous materials. To investigate the effect of the reaction time on the distribution of products, the hold time at each final temperature was varied at 15, 60, and 240 min, respectively. Condensable products were collected for further analysis by passing evolved gas through ice-cooled condensers.

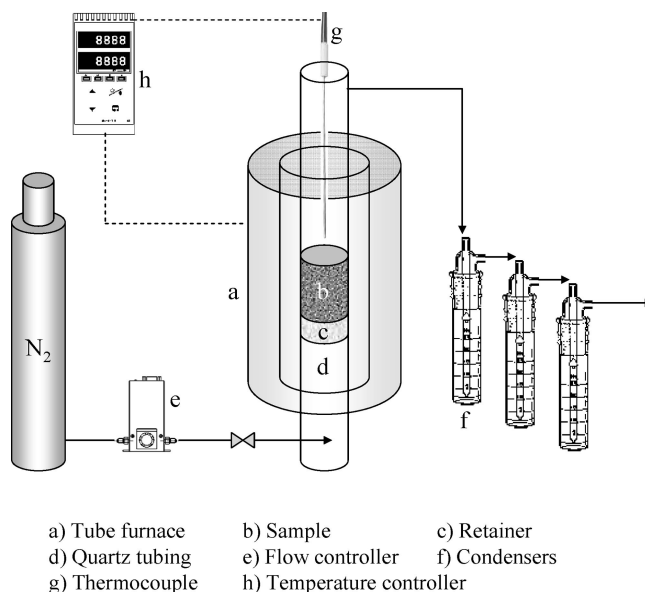


Figure 1. Schematic of the pyrolysis reactor setup.

2.4. Preparation of Activated Carbon. After pyrolysis, the char was removed, crushed, and sieved to a uniform size, ranging from 0.4 to 0.5 mm, and then kept in a dessicator for further activation via KOH, H₃PO₄, and CO₂ methods. Treatment with KOH was performed by mixing the sample with a concentrated solution of KOH in a beaker, with the weight ratio of KOH/char equal to 1.0. The sample was then evaporated at 80 °C for 24 h, and a dried mixture consisting of activated char (and KOH) was obtained.^{6,7}

Activation by H₃PO₄ was similar to that described elsewhere.⁵ The char sample was mixed with a 75% phosphoric acid aqueous solution, with a H₃PO₄/char mass ratio equal to 1.0. The slurry was dried at 60 °C for 24 h. All samples obtained were washed with deionized water. The sample was then poured to a beaker containing 250 mL of 0.1 mol/L HCl and stirred for 1 h. Finally, the sample was rinsed with hot water until the pH of the washing solution reached 6–7.^{11–14} CO₂ activation was accomplished by roasting pyrolyzed char under 100 mL/min of CO₂ at 400 °C for 30 min. The apparatus used was similar to that of the pyrolysis process described earlier.

2.5. Characterization of Activated Carbon. **2.5.1. Chemical Characterization.** Elemental analysis was carried out using a CHNS/O analyzer (Perkin Elmer PE2400 series II). Fixed carbon, volatile, and ash analyses were carried out using a thermogravimetric analyzer. When the sample was heated under an inert atmosphere to 850 °C, the weight loss during this step is a volatile component. The gas atmosphere is then switched to air to burn off fixed carbon, while the temperature is reduced to 800 °C. Finally, any residue left after the system is cooled to room temperature is considered as ash.

An X-ray diffractometer was used to investigate the surface inorganic components of the prepared activated carbons. The X-ray patterns were recorded under the scan rate of 0.1°/min. The surface organic functional groups were studied by Fourier transform infrared spectroscopy (Perkin Elmer System 2000 FT-IR). The spectra were recorded from a wavenumber of 400–4000 cm^{−1}.

2.5.2. Textural Characterization. The surface area and the porous texture of activated carbons were characterized using adsorption of nitrogen at −196 °C with the accelerated surface area and porosimetry system (ASAP 2020; Micro Meritics). The N₂ adsorp-

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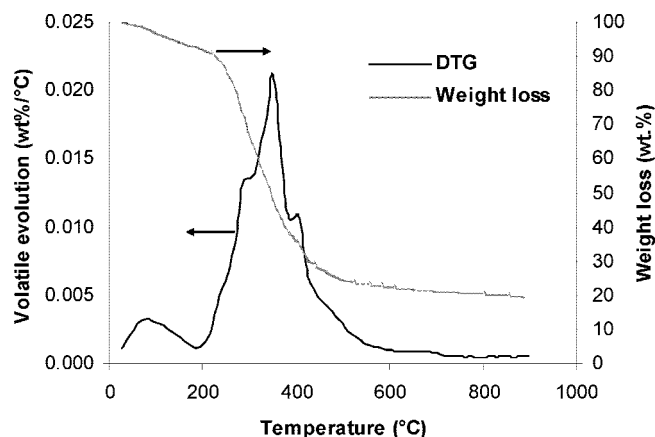


Figure 2. Pyrolytic thermogravimetric analysis of the residue showing weight loss and DTG plots.

tion-desorption isotherms were used to determine the following parameters: surface area [using the Brunauer–Emmett–Teller (BET) equation],¹⁵ total pore volume, total micropore volume, and total mesopore volume. The surface characteristics of samples were analyzed using scanning electron microscopy (JSM 5410, JELO). The instrument was operated under gold field emission with the accelerating voltage of 2500. Scanning was performed *in situ* on a carbon powder.

3. Results and Discussion

3.1. Thermal Degradation of Physic Nut Waste. Thermogravimetric analysis of the physic nut residue revealed that major thermal decomposition occurred around 250–450 °C as shown in Figure 2. Generally, biomass consists of hemicellulose, cellulose, lignin, and extractives. From pyrolytic differential thermogravimetric (DTG) curves, initial weight loss corresponds to moisture removal, followed by a second degradation event around 200–400 °C, where the evolution of light volatile compounds occurs from the degradation of cellulose and hemicelluloses. Degradation of lignin slowly takes place in a wide temperature range and lasts to higher temperatures. Thermal degradation of these individual components may be superimposed to simulate the overall degradation of the original biomass.¹⁶

3.2. Pyrolysis Yields. Thermal degradation of biomass results in solid, liquid, and gas products with the relative quantity mainly depending upon process parameters, such as sample size, reaction temperature, residence time, and reacting gas environment. The product distribution from the pyrolysis of physic nut waste with a particle size of 0.85–1.80 mm is displayed in Figure 3. The effect of the hold time on the apparent product yield was not significant because the shortest time of 15 min used in this work was appreciably long enough compared to typical devolatilization rates of biomass, in that most of the primary pyrolytic reactions were complete by that time. In addition, from previous thermogravimetric analysis, major decomposition processes of physic nut waste would have been over at the lowest tested temperature of 400 °C. Hence, a slow change of product yield is mainly resulting from secondary reactions at higher temperature. Yields of solid slowly decrease with temperature because of subsequent decompositions of the solid matrix at higher temperature, probably to liquid products, resulting in higher liquid yields at those conditions. Generally,

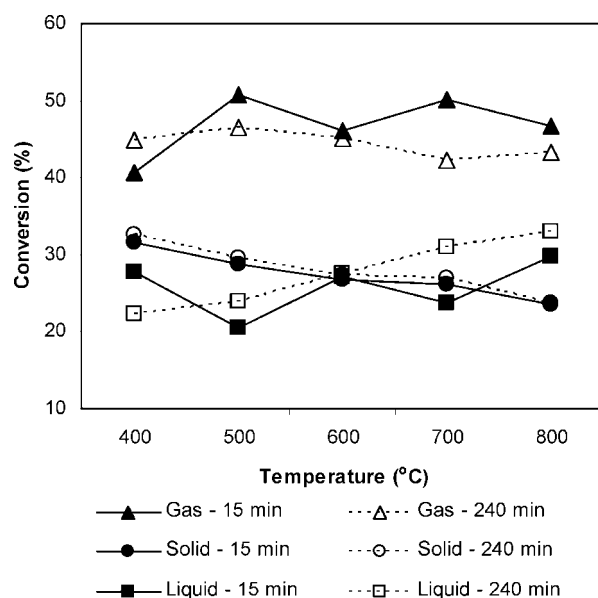


Figure 3. Product distribution from the pyrolysis of physic nut waste using hold times of 15 and 240 min.

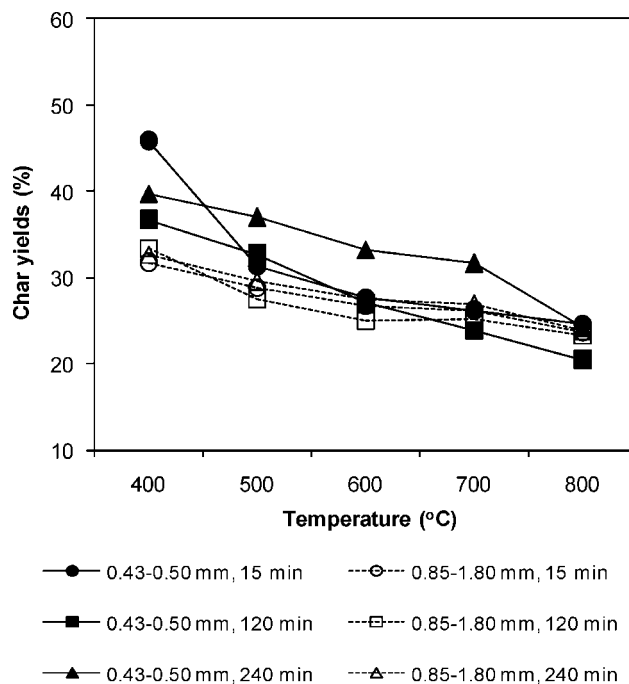


Figure 4. Char yields from the pyrolysis of physic nut waste.

yields of gas are highest, while solid yields are greater than liquid products, except at some high-temperature conditions.

Particle size exhibits less influence on the product quantity at higher temperatures as noticed from Figure 4, for the data on char yields. Char yields from a larger particle size of 0.85–1.80 mm were 5–15% lower than that of 0.43–0.50 mm at 400 °C, while the gap was narrower at higher temperatures. Generally, in view of heat- and mass-transfer limitations, the result should be opposite because larger particles may not be heated evenly and would require more time for mass transport through the particle. However, this is a slow-heating process as described earlier; therefore, these limitations are not applied. Thus, the variation on char yield may result from the nonuniformity of raw material, typical for bio-based material, such as physic nut waste. The chemical composition of small-particle waste may somewhat be different from that of larger ones. The

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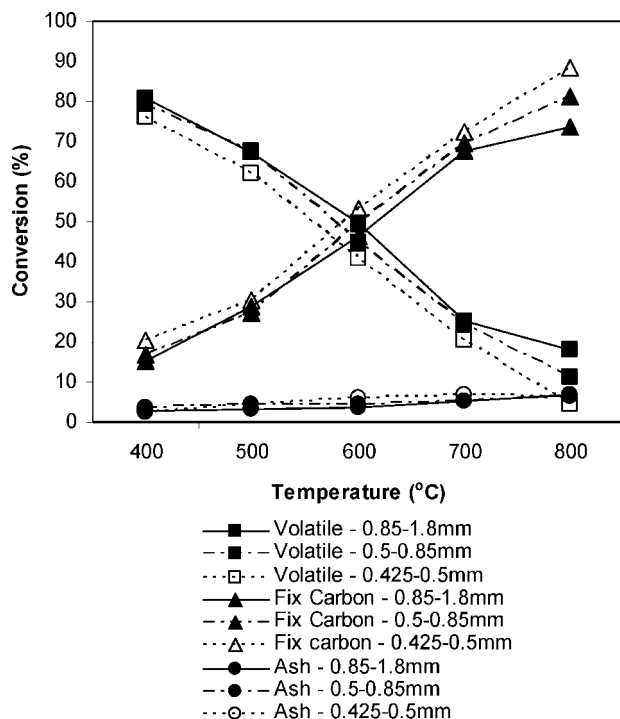


Figure 5. Components in char from the pyrolysis of physic nut waste using a hold time of 15 min.

waste sample was generated from the crushing of whole seed including its shell; therefore, larger particles tend to include more shell fraction, while the greater cake portion belongs to smaller particles. At a lower reaction temperature, some of the more stable components in small particles may not be readily decomposed, while at higher temperatures, most of these constituents can be thermally devolatilized, leaving a comparable amount of char.

For the production of high-quality activated carbon, a greater surface area along with higher fixed carbon content is preferable. Although similar in quantity, the quality of chars obtained at different operating conditions is different in terms of fixed carbon, volatiles, and ash contents as displayed in Figure 5. Smaller particles tend to yield char with high fixed carbon and low in volatiles when compared at the same reaction temperature. The highest char fixed carbon value of 88.24% was obtained by pyrolysis of 0.43–0.50 mm particles at 800 °C for 15 min with relatively low volatiles of 4.30%. Higher pyrolysis temperatures may be applied to obtain a greater fixed carbon content, but the cost of operation at high temperature as well as greater carbon burn off and the possibility of pore closure from sintering would limit such effort.

3.3. Activation of Physic Nut Waste Char. Although any biomass materials may be thermochemically converted and activated to become porous carbons, the physicochemical properties of the products can be significantly varied depending upon biomass species, char preparation, and activation methods. Comprehensive characterization and testing on obtained activated products is important to identify the proper pyrolysis and activating conditions as well as optimizing the overall process.

3.3.1. Pore Structure. The BET surface area and mesopore volume data of activated carbons from physic nut waste char with an initial particle size of 0.43–0.50 mm are summarized in Figure 6 along with the baseline results of char prior to the activation. It can be seen that various degrees of improvement of surface area and mesopore volume may be achieved after activation. Generally, the specific surface areas of activated char are increased by the chemical and physical modifications. The

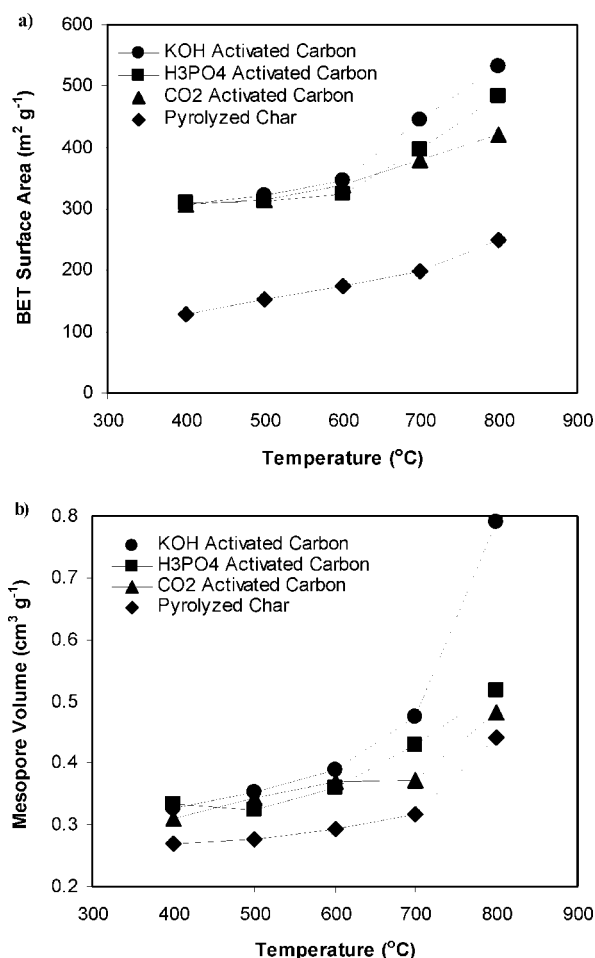


Figure 6. Surface properties of activated carbon and original char: (a) BET surface area and (b) mesopore volume.

BET surface area is considerably increased because of the blocking of the narrow pore by the surface complexes introduced by KOH, H₃PO₄, and CO₂ treatments. The highest surface area of 532.30 m² g⁻¹ may be achieved via KOH activation. Lesser improvement is observed for the activation with H₃PO₄, while the physical CO₂ method yielded a modest increase to 420.20 m² g⁻¹ from 249.60 m² g⁻¹ in the original char. Activated chars from lower pyrolysis temperatures displayed poor surface properties because of their high volatile contents.

Typically, any practical activated carbon should have a BET surface area of more than 500 m² g⁻¹.¹⁷ From the analysis above, it may be proposed that only KOH-activated chars obtained from the pyrolysis of a 0.43–0.50 mm residue at 800 °C for 15 and 120 min (not reported here) may be considered as functional activated carbon. It should be noted that the KOH-activated char from the same condition but with a hold time of 240 min has a surface area lower than 500 m² g⁻¹, which may be due to sintering of the pore at high temperature and long heating time.

According to Meldrum and Rochester,¹⁸ the stability of the graphite basal planes is high; therefore, oxygen surface groups are expected to be located at the edges of the basal planes, which are relatively weak sites of carbon structure, and oxidation progresses slowly into the basal planes. In this work, the isotherms and porosities of activated char indicate that some of the pores were blocked by oxide functional groups introduced

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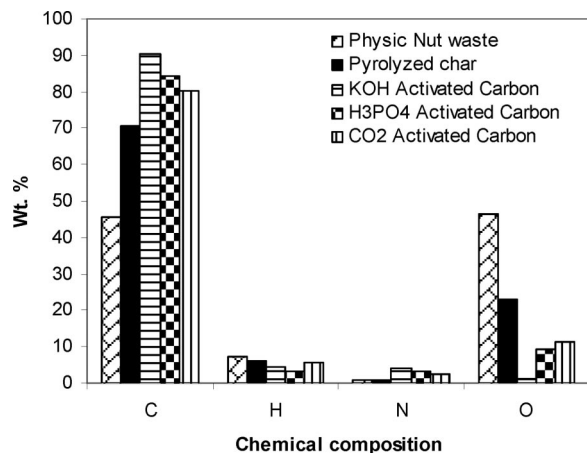


Figure 7. Chemical composition of raw material and activated carbon products.

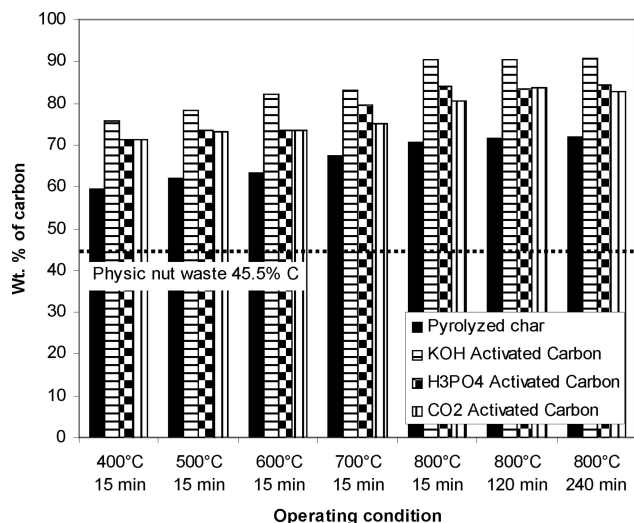


Figure 8. Carbon content in raw material and activated carbon products.

by the activated treatment. The increase of the surface area was mainly attributed to the increase of the mesopore volume. The difference of the total pore volume of $0.265 \text{ cm}^3 \text{ g}^{-1}$ was on par with the increase of the mesopore volume of $0.348 \text{ cm}^3 \text{ g}^{-1}$ after chemical modification by KOH. Also, the difference of 0.075 and $0.040 \text{ cm}^3 \text{ g}^{-1}$ were due to the increase of the mesopore volume of $0.143 \text{ cm}^3 \text{ g}^{-1}$ for the activation via H_3PO_4 and CO_2 gas. Results from testing physic nut waste with a larger particle size (not shown here) are similar but with less improvement on surface properties.

3.3.2. Chemical Composition of Activated Carbons. Chemical compositions of activated carbons obtained in this work by impregnation with KOH and H_3PO_4 as well as CO_2 activation are shown in Figure 7 along with those of starter materials. The data shown here are for the original residue particle size of $0.43\text{--}0.50 \text{ mm}$ and pyrolyzed at 800°C for 15 min. As expected, all processed samples have much higher contents of carbon and lower percentages of oxygen and hydrogen compared to the initial biomass and its associated char materials. Both chemical and CO_2 activations strongly promote deeper carbonization with a greater effect by prior methods, especially for those pyrolyzed at a high temperature of 800°C and activated with KOH (Figure 8). As a matter of fact, the combination of both chemical and physical activation may accelerate the chemical changes in material and enable the removal of hydrogen and oxygen, resulting in supplemented carbon content.

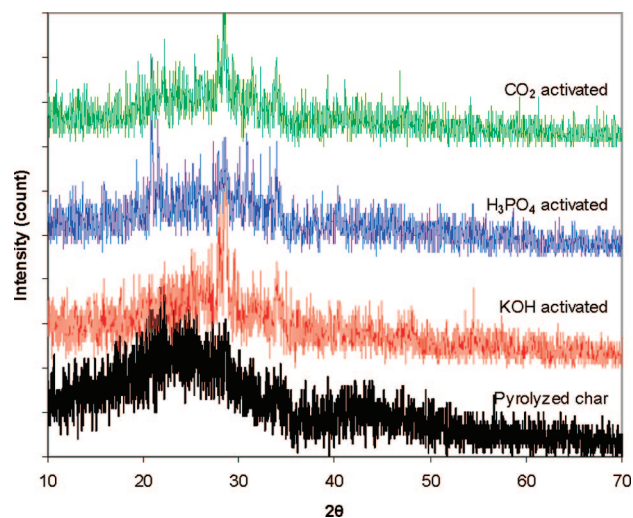
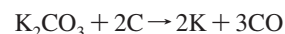
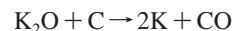
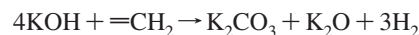


Figure 9. X-ray diffraction analysis of pyrolyzed char and activated carbons.

The effects of KOH on the carbonization of carbonaceous materials have been reported by several authors.^{13,19–21} These studies suggested that enhancing the formation of active carbons from physic nut waste char, after the reaction with KOH, may occur by the oxygen of the alkali, which can remove cross-linking and stabilizing carbon atoms in crystallites. Potassium metal, obtained at the reaction temperature, may intercalate and force apart the separate lamellae of the crystallite. Removal of potassium salts from the internal volume of the char by washing creates the mesoporosity in this newly formed structure. However, a further reaction between KOH and carbon of the mesoporous structure formed at a previous stage may destroy the mesoporous structure and enlarge the volume of pores. The following reactions may take place during the activation processes:^{22–24}



It has been described that the activation by phosphoric acid may be incomplete, resulting in partial chemical structural alterations. Phosphoric acid functions in two ways: (1) as an acidic catalyst in promoting bond cleavage reactions and formation of cross-links and (2) by being able to combine with organic species to form phosphate linkages, such as phosphate and polyphosphate esters, that can serve to connect and cross-link biopolymer fragments.

The pore quantity and radii distribution of the impregnated activated carbon largely varies with different chemicals used. Thus, the most important difference between the activation mechanism with KOH and H_3PO_4 is that, whereas the first mechanism removes and avoids the cross-linking, stabilizing

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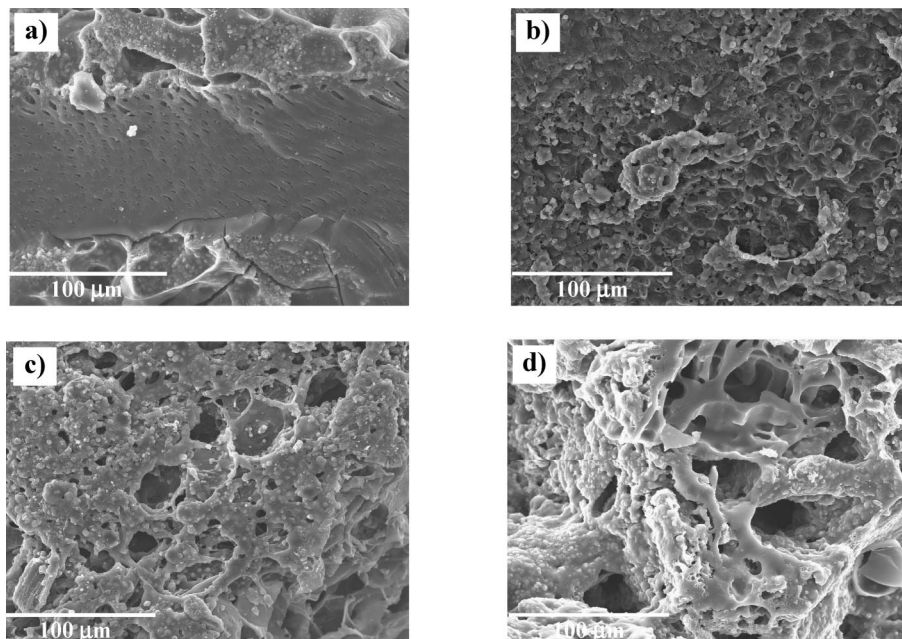
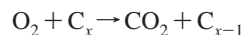
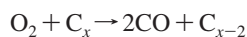
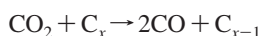


Figure 10. Scanning electron micrograph of (a) char without activation and char activated by (b) CO₂, (c) H₃PO₄, and (d) KOH.

the carbon atoms in crystallites, the second mechanism involves an excessive cross-linking by acid catalysis.

For physical activation, to increase the surface area, the carbon is activated by the action of carbon dioxide. The oxidizing gas attacks the more readily oxidizable portion of the char, resulting in the development of the porous structure and the extensive internal surface area.^{25,26} Typically, the reactions may be presented by



3.3.3. X-ray Diffractometer (XRD) and Scanning Electron Microscope (SEM). It is generally accepted that pore structure development is influenced by many factors, including inorganic impurities and the initial structure of the carbon precursor. Therefore, the XRD and SEM images were obtained for all samples in this study and displayed in Figures 9 and 10. The appearance of a broad peak centered at the 2θ angle of 28° in the X-ray diffractograms of pyrolyzed char and activated carbon indicated the presence of silica. Diffractograms of carbon activated by KOH, H₃PO₄, as well as CO₂ were quite similar, while the graphitic basal planes at a 2θ angle of 43° could only be seen in the spectrum of pyrolyzed char but not in the activated carbon samples.

Generally, the wood surface has a relatively smooth structure with some pores and occasional crevices and also covered with silica agglomeration. However, in this work, the physic nut residue was obtained from an oil-extraction process using a twin screw extruder; thus, there was rupturing of wood tissues in the waste structure. During pyrolysis, the char may be evolved through a liquid phase. The surface showed relatively smooth regions as well as cracked and pitted morphology. The presence of small pores on the surface showed that char was starting to develop an elementary pore network (Figure 10a). From parts

b–d of Figure 10, it can be clearly seen that physical and chemical activation resulted in a porous structure and the opening of pores on the surface of all activated carbon. According to the International Union of Pure and Applied Chemistry (IUPAC),²⁷ pores on activated carbons are classified by their sizes into three groups: macropores having an average diameter of greater than 50 nm, mesopores with a diameter of 2–50 nm, and micropores having an average diameter of less than 2 nm. Nitrogen adsorption isotherms of the physic-nut-waste-activated carbons indicated that they were mainly mesopores.

The different pore structures of the activated carbon prepared from either physical (using CO₂) or chemical (using KOH and H₃PO₄) activation are observed, which depend upon different reaction mechanisms. Activation with CO₂ at 400 °C mainly developed pores of a similar shape and size and evenly distributed throughout the particle. The mesopores seemed to directly expose the surface of the activated carbon. On the contrary, in char activated by KOH and H₃PO₄, pores are irregular, of different shapes and sizes, and the macropores seem to be connected to mesopores, especially for the KOH-activated case. The KOH molecule is smaller than that of H₃PO₄; thus, it diffused faster into the pores of the carbon. Consequently, the reaction with KOH was faster than that with H₃PO₄, aiding in the creation of the porous structure. Overall, the higher surface area and mesopore volume of the chemically activated carbons reported from the BET method (section 3.3.1) corresponded well with the observation from SEM micrographs.

3.3.4. Fourier Transform Infrared (FTIR) Spectrometer. The adsorption capacity of activated carbon depends upon porosity as well as the chemical reactivity of functional groups at the surface. This reactivity creates an imbalance between forces at the surface as compared to those within the body, thus leading to molecular adsorption by the van der Waals force. Knowledge on surface functional groups would give insight to the adsorption capability of the produced activated chars. FTIR spectra were collected for qualitative characterization of surface functional

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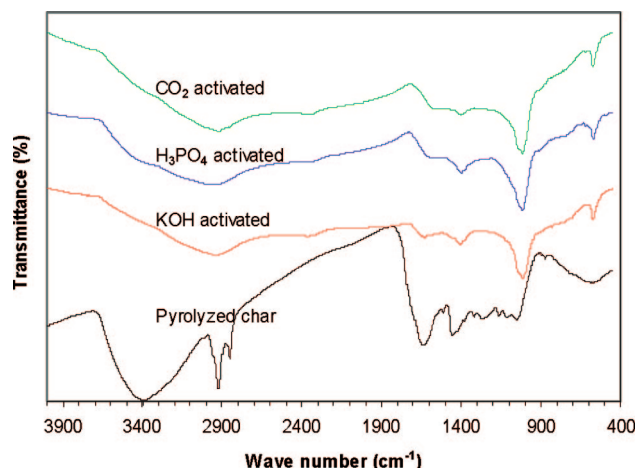


Figure 11. FTIR spectra of pyrolyzed char and activated carbons.

groups of porous carbons activated by both physical and chemical methods. Figure 11 shows that the functional groups of activated carbon differ significantly from those of pyrolyzed char.

The spectrum from char at 3393 cm^{-1} indicated the presence of the -OH group of phenol. The methylene group is detected by -CH stretching at a wavenumber of 2924 cm^{-1} . The aldehyde group of -O-CH_3 is found around 2853 cm^{-1} . Strong bands at 1641 cm^{-1} indicate C=O stretching of carboxyl or carbonyl groups. Methyl or amine groups are shown by a peak around $1385\text{--}1380\text{ cm}^{-1}$. The band from 1200 to 1000 cm^{-1} is the fingerprint of syringyl units. Aldehyde and derivatives of benzene are detected by peaks at 875 and 761 cm^{-1} .²⁸

FTIR spectra of char activated by different methods are quite similar. The peak around 2920 cm^{-1} is thought to be of the methylene group. The aldehyde group is also detected by a peak at 2848 cm^{-1} . The band around $1590\text{--}1500\text{ cm}^{-1}$ is assigned to ring vibration in a large aromatic skeleton generally found in carbonaceous material, such as activated carbon.^{29,30} Peaks around $1450\text{--}1320\text{ cm}^{-1}$ are an indication of the presence of pyrones and aromatic groups. For carbon prepared by H_3PO_4

activation, the band at $1420\text{--}1350\text{ cm}^{-1}$ could also be caused by phosphorus-containing groups.^{20,21} The strong bonds located around 1010 and 832 cm^{-1} are attributed to asymmetric and symmetric stretching of the Si-O band.

4. Conclusions

Preparation of activated carbon from pyrolyzed physic nut waste char was performed in a laboratory-scale facility. The data obtained indicated that activated carbon with favorable physicochemical properties may be produced via several methods described earlier. Carbon contents of activated materials were $80.4\text{--}90.3\%$, depending upon the activation method, and notably higher than preactivated char, which exemplified the crucial role of this process. The activated carbon prepared by chemical activation of the pyrolyzed physic nut residue at 800°C with KOH attained a maximum BET surface area of $532.3\text{ m}^2\text{ g}^{-1}$, while the surface area of those activated with H_3PO_4 and CO_2 were lower. Mesopore and total pore volumes were also significantly enhanced in the same trend. Pores of activated carbon from the physic nut residue were found to be mainly mesopores with irregular, different shapes and sizes for char ones activated by KOH and H_3PO_4 , and the macropores seemed to be connected to mesopores, especially for a case of KOH activation. FTIR analysis of the surface of pyrolyzed char indicated main functional groups that are significantly different than those of activated materials, which suggests a possible enhancement on the adsorption capability of the latter ones. Functional groups on each activated carbon are quite similar even with different activation processes.

Further testing on the adsorption capacity of prepared activated carbon would confirm the feasibility on the production of quality activated carbon from plant oil waste, such as physic nut, which would promote sustainable usage of alternative fuel, considered as green energy, and ultimately reduce the dependency of the world on fossil fuel.

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