Investigation of Pyrolyzed Chars from Physic Nut Waste for the Preparation of Activated Carbon

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Abstract

Fixed bed pyrolysis of physic nut waste was conducted to investigate the influence of different operating conditions, such as sample size, final temperature and hold time, on properties of the pyrolyzed chars. The obtained chars were characterized by a thermogravimetric analyzer (TGA) for proximate analyses and by Brunauer-Emmett-Teller (BET) for determination of their accelerated surface area. The surface morphology of char was investigated using scanning electron microscopy (SEM). For chemical characterization, an X-ray diffractometer (XRD) and a Fourier transform infrared spectrooscope (FTIR) were used to identify inorganic components and surface organic functional groups of the char. In this work, the FTIR analysis indicated the existence of phosphonate groups, carboxyl groups and amine groups on char surface. The XRD pattern of the surface also verified the presence of graphite as main carbon structure. The conditions yielding char with maximum BET surface area of 249.60 m²·g⁻¹ and high fixed carbon are final temperature of 800°C, hold time of 15 minutes, and heating rate of 20°C/min for 0.425-0.5 mm particle. Generally, high temperature pyrolysis of raw materials with short hold time results in char with favorable smooth, porous surface with large cavities.

Key words: Pyrolysis, Physic Nut Waste, Activated Carbon

1. Introduction

Burning of biomass has been carried out worldwide since the ancient times for cooking and heating purposes. However, since biomass usually contains high moisture content, and has low density, there are several inherited difficulties with regard to transportation, storage, and usage of biomass without any pretreatment. Therefore, some thermal conversion methods such as pyrolysis, gasification, and carbonization have been carried out to produce enhanced fuel products from biomass. In this respect, biomass is subjected to various decomposition processes. Particularly, the pyrolysis process, by which solid, liquid, and gaseous products are obtained from biomass as a result of heat treatment under non-oxidizing condition and have widely been applied to a number of biomass species [1-3].

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In many tropical regions, special interest has been shown in the use of physic nut (Jatropha curcas L.) for this purpose, especially since it is drought resistant and can potentially be extracted for bio-oil, without competing with food production. Successful use of physic nut seed oil in car engines has been reported by several groups [4, 5] which promotes the heavy cultivation of this plant in many countries and may lead to the problem with its associated waste from extraction.

An environmental friendly option to alleviate this problem may be the conversion of this waste into a value added product such as activated carbon. Typically, this transformation may be done through pyrolysis process where cellulose and hemicelluloses in biomass would mostly be decomposed to volatile products, while lignin content is responsible for the conversion to solid char [6]. More specifically, activated carbon formation consists of a charring or carbonization step in which most of biomass materials (and much of the carbon) is volatilized at high temperature (around 400-800°C). Char is usually first pre-oxidized at 100 to 250°C, to prevent the biomass from becoming biopolymer during charring and collapsing of the pore structure.

The fine pore structure is formed in an activation process. During chemical activation, the char is impregnated with some chemicals and then fired at high temperatures. The activating chemical corrodes the carbon to form the pore structure. Chemical activation also alters the carbon surface. Activation chemicals are usually strong acids, bases or corrosives such as phosphoric acid, sulfuric acid, zinc chloride, potassium hydroxide, potassium sulfide, or potassium thiocyanate.

The surface chemistry of the activated carbon is strongly influenced by the activation process and subsequent chemical treatment. The surface contains abundant oxygen and hydrogen groups which can decompose to CO₂ and water. The advantage of surface complexes causes activated carbon to be a good absorber of many gases and aqueous chemicals. The non-selective absorption of many chemicals makes activated carbon an excellent absorber in poisoning or environmental contaminant applications.

However, for the case of biomass, the condition during pyrolysis as well as plant species may have significant effects on char and, after activation, the produced activated carbon when compare with better defined material such as coal [7, 8]. As a result, goals of this work are to investigate the influences of different operating parameters, such as initial material size, pyrolysis temperature, and hold time, on the quantity and quality of pyrolyzed chars from physic nut waste by thoroughly characterization of the product using several analytical procedures and to suggest the optimum pyrolysis condition which yields the most favorable char characteristic suitable for subsequent activation.

2. Experimental Procedure

2.1 Sample preparation

Extracted physic nut wastes (grain mill with Hatz engine) from local operation were first dried at 60°C for 24 hours to reduce their moisture content. The dried samples were then crushed and sieved to different size fractions (0.425-0.5, 0.5-0.85, 0.85-1.8 and 0.85-3.6 mm). In this study, only the size fraction of 0.425-0.5 mm is subjected to complete experimentation. The chemical contents of physic nut waste sample were further identified using Tappi T203 and T222 standard methods. The major components of raw material are shown in Table 1, which are cellulose, hemicellulose, lignin and other unidentified components.
Table 1. Chemical components analysis of physic nut waste.

<table>
<thead>
<tr>
<th>Component</th>
<th>Physic nut composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td>33.54</td>
</tr>
<tr>
<td>Cellulose</td>
<td>50.34</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>12.84</td>
</tr>
<tr>
<td>Total</td>
<td>96.72</td>
</tr>
</tbody>
</table>

2.2 Experimental setup and procedure

The pyrolysis of physic nut was carried out using a packed-bed reactor. The system consisted essentially of a quartz tube reactor (height = 400 mm, inside diameter = 12 mm, and wall thickness = 0.5 mm) with a sample retainer made of quartz wool, a cooling system for the separation of water and condensable organic vapors (tar), and a gas cleaning/drying system followed by gas-measurement devices. For every trial, approximately 5.5 g of sample was placed into the reactor. Prior to heating, inert purging gas (high purity nitrogen) was provided from the bottom of the reactor at 100 mL/min to maintain the pyrolysis atmosphere. The ceramic tube furnace was then heated at a heating rate 20°C/min to the final pyrolysis temperature of 400, 500, 600, 700 and 800°C, respectively, each with hold times of 0.25, 2 and 4 hours, then left to natural cool down before dissembled to recover char samples.

2.3 Analytical methods

The pyrolyzed samples were subjected to battery of analyses in order to evaluate the feasibility of using them as raw materials for activated carbon production. The influence of various pyrolysis conditions were recorded by thermogravimetric analyzer, BET surface area, scanning electron microscope, X-ray diffractometer, and Transmission Fourier-transform infrared spectroscopy as discussed below.

2.3.1 Thermo gravimetric analyzer (TGA)

Thermo gravimetric analyzer (METTLER TOLEDO : TGA/SDTA 851®) was used to
carry out the proximate analysis which was expressed in terms of moisture, volatile matter, fixed carbon, ash contents and char yield [9]. A sample of extracted physic nut seed was heated from room temperature to 100°C in an inert atmosphere until complete dehydration and followed by decomposition at 850°C for 10 minutes to determine the quantity of volatile matters. The atmosphere was then changed to be oxidizing with the introduction of air while the sample was cooled to 800°C and maintained at this temperature until its weight remain unchanged. The weight loss during this period was due to the reaction of the fixed carbon with oxygen and the resulting residue was ash. The sample weight losses during pyrolysis for different final temperature and hold times were continuously recorded by TGA data acquisition [10].

2.3.2 Porous properties of chars
Characterization of the pyrolyzed chars was determined by nitrogen adsorption at -196°C with the accelerated surface area and porosimetry system (ASAP 2020: Micro Meritics). The BET surface area was calculated from N₂ adsorption isotherms by using the Brunauer-Emmett-Teller (BET) equation [11].

2.3.3 Surface property
A scanning electron microscope, JSM 5410 (JELO), was used to verify the presence of porosity on the char surfaces. The magnifications of SEM were selected as ×50, ×500, and ×5000. In this study, elemental determination of the char surfaces was obtained with energy-dispersive X-ray spectroscopy (EDS Model INCA 300).

2.3.4 Chemical characterization
An X-ray diffractometer was used to investigate the surface inorganic components of the chars. The X-ray patterns were recorded in the scan range of 2θ = 10-70° at scan rate of 0.1°/min. The surface organic functional groups were studied by Transmission Fourier-transform infrared spectroscopy (PERKIN ELMER System 2000 FT-IR). The spectra were recorded from wave number of 450 to 4000 cm⁻¹.

3. Results and Discussion

3.1 Proximate analysis
Starting material for activated carbon production is expected to be high in carbon but low in volatile and ash contents. Results of the proximate analyses of chars from extracted physic nut waste with a particle size range of 0.425-0.5 mm, pyrolyzed at different pyrolysis temperatures for a hold time of 15 min and at 800°C for various hold times are summarized in Table 2.

| Table 2 Proximate analysis of the char prepared at different temperatures and various times |
|--------------------------------------------------|------------|------------|------|
| Pyrolysis condition | Volatile Matter (%) | Fixed Carbon (%) | Ash (%) |
| 400°C-15min | 79.20 | 18.86 | 1.50 |
| 500°C-15 min | 65.01 | 30.70 | 3.28 |
| 600°C-15 min | 33.32 | 62.44 | 3.93 |
| 700°C-15 min | 15.22 | 79.32 | 4.41 |
| 800°C-15 min | 4.34 | 90.01 | 4.87 |
| 800°C-15 min | 4.34 | 90.01 | 4.87 |
| 800°C-2 hr | 6.29 | 88.06 | 4.78 |
| 800°C-4 hr | 11.57 | 83.11 | 4.69 |
As pyrolysis temperature increased from 400 to 800°C, the volatile content of chars decreased progressively from 79.20 to 4.34% whilst both the ash content and the fixed carbon increased. This trend was expected because increased devolatilization temperature during pyrolysis promoted the release of volatiles from breaking of weaker bridges and bonds in organic matrices as well as enhanced the condensation and collapsing reactions of organic matters in the sample to become char with predominantly fixed carbon. For the char pyrolyzed at 800°C for different times, changes in the fixed carbon contents and the volatile matter were relatively small, because large amount of volatiles had already been early released at that high temperature 800°C. Consequently, chars pyrolyzed from physic nut are of high fixed carbon and low ash contents which are favorable for the preparation of activated carbons.

3.2 Char yield

Appreciable amount of char (with high fixed carbon) left after pyrolysis is an important factor to determine optimum operating condition. The yield of chars can be calculated from the sample weight after pyrolysis to its initial weight. Figure 1 shows the effect of temperature and retention time on char yield. In this work, the term of char is used collectively to represent the solid residue that remained after pyrolysis.

![Fig. 2 Yield of chars versus hold time at different pyrolysis temperatures](image)

The trend was decreasing char yield as a pyrolysis temperature increased for a particular hold time. The differences in char yields became less for increasing hold time since more volatiles were released, leaving only small quantities of volatiles available for evolution at the end of long hold times. In general percent char yields increase with decrease hold time and final temperature. At low pyrolysis temperature, the effect of hold time on char yield was more significant than at high temperature. For the case study, at 400°C the char yield was dropped 9% as a hold time increased from 15 minutes to 4 hours. Although, at 800°C the yield decreased about 3% for the same increased hold time suggesting that decomposition reactions which release volatile matters would have been rapid at such high temperature and mostly finished in short time.

3.3 Chemical characteristics

3.3.1 Identification of surface functional group

Fewer functional groups were detected as observed from the FTIR spectra of the char
shown in Figure 3, indicating that the surface function groups of physic nut waste significantly experienced chemical changes during pyrolysis. The spectrum displays the following peaks. The absorption peaks around wavenumber of 3500-3000, 1512, and 1383 cm\(^{-1}\) are indicative of the existence of amine groups. The spectrum also displays the adsorption peaks at wavenumber of 3600-3200, 1641, and 1270 cm\(^{-1}\), corresponding to carboxyl groups. The phosphonate groups show some characteristic absorption peaks around wavenumber of 1159 cm\(^{-1}\) (P-O stretching) and 1055 cm\(^{-1}\) (P-OH stretching) [15-18].

![Fig. 3 FTIR spectra of pyrolyzed char from physic nut waste](image)

**3.3.2 XRD characterization**

X-ray diffractometer was used to record X-ray diffraction spectra from char sample by scanning over the angular 2\(\theta\) range of 10-70\(^{\circ}\) and intensity at various degrees was displayed in Figure 4. There are two broad diffraction peaks around 2\(\theta\) = 23\(^{\circ}\) and 2\(\theta\) = 43\(^{\circ}\) in a spectrum which confirm the structure of graphitic basal plans of char crystallite in the low angle region ((002) peak of graphite) and radial spread of crystalline structures in high angle region ((100) peak of graphite) [19]. Hence, the chars obtain are believed to be in the form of graphite.

![Fig. 4 X-ray diffraction pattern of the char pyrolyzed from physic nut waste](image)
3.4 Surface properties

The SEM images of physic nut chars produced under different hold time and pyrolysis temperature are exhibited in Figures 5 and 6. The char samples depicted in these figures were all produced in the reactor under nitrogen gas. The comparison of char particle under retention time of 15 minutes and various temperature of pyrolysis is exhibited in Figure 5. These photos revealed changes in surface morphology of chars as a function of retention time and temperature of pyrolysis process. As shown, at low temperature, the surface of chars was found to be smooth and homogeneous. However, after 700°C of pyrolysis, surface morphological changes were evident. The indication of volatile matter loss was observed through forming of a system of advanced pore structure. Due to this well-developed pores, the chars possessed high BET surface area.

Fig. 5 SEM images of physic nut chars obtained at different pyrolysis temperature of:
(a) 400°C, (b) 500°C, (c) 600°C, (d) 700°C, and (e) 800°C
The SEM images of chars at different hold time and the same pyrolysis temperature of 800°C (Figure 6) indicates the existence of little pores at 4 hours of retention time and a great number of large pores at low hold time.

![Fig. 6 SEM images of chars pyrolyzed at 800°C with different hold time from: (a) 15 minutes and (b) 4 hours](image)

The surface area of chars produced at various retention time and final temperature are shown in Table 3. It is evident that increasing pyrolysis temperature, from 400 to 800°C, resulted in greater volatile matters released from the process thereby promoting in the development of some new pores, and hence the BET surface areas increased progressively. But increasing hold time at the same final temperature adversely decreased the total surface area because some of the pores were being sealed off as a result of sintering at rigorous environment for longer period of time.

<table>
<thead>
<tr>
<th>Pyrolysis condition</th>
<th>BET surface area (m²·g⁻¹)</th>
<th>Total volume (cm³·g⁻¹)</th>
<th>Mesopore area (m²·g⁻¹)</th>
<th>Mesopore volume (cm³·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400°C-15min</td>
<td>127.70</td>
<td>0.081</td>
<td>114.84</td>
<td>0.269</td>
</tr>
<tr>
<td>500°C-15min</td>
<td>153.08</td>
<td>0.094</td>
<td>130.33</td>
<td>0.277</td>
</tr>
<tr>
<td>600°C-15min</td>
<td>174.49</td>
<td>0.097</td>
<td>155.16</td>
<td>0.294</td>
</tr>
<tr>
<td>700°C-15min</td>
<td>198.40</td>
<td>0.106</td>
<td>161.35</td>
<td>0.318</td>
</tr>
<tr>
<td>800°C-15min</td>
<td>249.60</td>
<td>0.143</td>
<td>188.79</td>
<td>0.442</td>
</tr>
<tr>
<td>800°C-15min</td>
<td>249.60</td>
<td>0.143</td>
<td>188.79</td>
<td>0.442</td>
</tr>
<tr>
<td>800°C-2 hr</td>
<td>234.40</td>
<td>0.132</td>
<td>181.10</td>
<td>0.406</td>
</tr>
<tr>
<td>800°C-4 hr</td>
<td>214.72</td>
<td>0.115</td>
<td>175.63</td>
<td>0.387</td>
</tr>
</tbody>
</table>

4. Conclusion

Chars from pyrolysis of extracted physic nut wastes could be developed into effective absorbents of activated carbon. The results of proximate analyses showed that the pyrolyzed chars possess high fixed carbon and high BET surface area but low volatile matter and moisture, which are favorable as raw material for activated carbon production. Increase in pyrolysis temperature and hold time resulted in greater fixed carbon percentages but also at the cost of reduction on char yields. Although, at a high temperature, the effect of retention time on the char yield was less significant.

The hold time and pyrolysis temperature are two important parameters of the pyrolysis process. At a high temperature of 800°C, increase in pore area was obvious but sintering effect of char at prolonged residence time may quickly sealed of those newly formed pores.
At a low pyrolysis temperature of 400°C, pore development was poor due to insufficient energy to release the volatile matter.

For the conditions performed in this work, the favorable settings for producing chars with a maximum BET surface area of 249.60 m²·g⁻¹ were pyrolysis to a final temperature of 800°C and holding at this temperature for 15 minutes. Additional works are being carried out to activate and test the adsorption performance of activated carbon from respective chars.

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