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Preparation and characterization of activated carbon from sugarcane bagasse by physical activation with CO\textsubscript{2}gas

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Abstract. A series of experiments have been conducted to study the effects of different carbonization temperatures (400, 600, and 800\textdegree C) on characteristics of porosity in activated carbon derived from carbonized sugarcane bagassechar at activation temperature of 800\textdegree C. The results showed that the activated carbon derived from high carbonized temperature of sugarcane bagassechars had higher BET surface area, total volume, micropore volume and yield as compared to the activated carbon derived from low carbonized temperature. The BET surface area, total volume and micropore volume of activated carbon prepared from sugarcane bagassechars obtained at 800\textdegree C of carbonized temperature and activation time of 120 min were 661.46 m\textsuperscript{2}/g, 0.2455 cm\textsuperscript{3}/g and 0.1989 cm\textsuperscript{3}/g, respectively. The high carbonization temperature (800\textdegree C) generated a highly microporous carbon with a Type-I nitrogen adsorption isotherm, while the low carbonization temperature (400 and 600\textdegree C) generated a mesoporous one with an intermediate between types I and II nitrogen adsorption isotherm.

1. Introduction

Activated carbons with highly developed surface area are usually used worldwide for water treatment, wastewater reclamation, gas purification and also as catalyst support [1, 2]. Activated carbons 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 [3]. In the recent years, many other agricultural by-products have been used as sources for activated carbons. Agricultural biomass wastes have proved to be promising raw materials for the production of activated carbons because of their availability at a low price, abundantly available, and renewable resources [4]. They were used for the production of activated carbon due to high carbon content, a high adsorption capacity, high density and considerable good mechanical strength. They also have low ash content which is ideal for creating highly porous structures within the activated carbon matrix. Many agricultural by-products such as coconut shell [5, 6, 7], grain sorghum [8], coffee bean husks [9], rubber wood sawdust [10], chestnut wood [11], and fruit stones [12], have been discovered to be suitable precursors for activated carbon due to their high carbon and low ash contents.

In general, there are two main steps for the preparation of activated carbon: (1) the carbonization of raw materials below 800\textdegree C, in the absence of oxygen, and (2) the activation of carbonized product (char), either using physical or chemical activation methods [13]. Generally physical activation is a two-step process which involves carbonization of raw materials followed by activation of the resulting char at elevated temperature in the presence of suitable oxidizing gases such as carbon dioxide, steam,
air or their mixtures. In the chemical activation process, both steps are carried out simultaneously, with the precursor being mixed with chemical activating agents. In chemical activation, dehydrating reagentssuch as phosphoric acid, sulfuric acid, zinc chloride, potassium hydroxide are used to impregnate the raw materials [14, 15, 16]. Chemical activation offers several advantages which include single step activation, low activation temperatures, low activation time, higher yields and better porous structure. However, the process involves a complex recovery and recycle of the activating agent, which generates liquid discharge that demands effluent treatment.

Sugarcane bagasse (SCB) is suitable for preparing activated carbons due to their excellent natural structure and low ash content. SCB is a byproduct of sugarcane industries obtained after the extraction of juice for production of sugar. Conversion of sugarcane bagasse into activated carbons which can be used as adsorbents, ion exchange, carbon molecular sieve, catalyst would add value to these agricultural commodities, help reduce the cost of waste disposal, and provide a potentially cheap alternative to existing commercial carbons. Studies on CO$_2$ activation of sugarcane bagasse have not been reported in literature and hence the present study attempts to prepare activated carbon with well-developed porosity. The aims of this work were to utilize SCB, biomass waste, for the preparation of activated carbon by physical activation using CO$_2$ gas as an activating agent. There are several critical parameters in the preparation of activated carbon that would affect its structure, one of which is carbonization temperature. The effects of carbonization temperature on the physico-chemical characteristics of the activated carbon were studied in order to obtain high adsorption capacity and surface area of the product. The one-step physical activation process using CO$_2$ gas is desirable due to lower energy consumption, capital expenditure, processing time that can significantly improve the process economics.

2. Methodology

2.1. Materials

Sugarcane bagasse used as raw materials to produce activated carbon in this study was obtained from sugarcane industries in Bantul, D.I. Yogyakarta province. The starting materials were manually chosen, cleaned with deionized water, dried at 110°C for 48 h and ground with a roller mill to obtain samples of 1–2 mm particle size. The schematic diagram of the experimental setup for the preparation of activated carbons using physical activation using CO$_2$ was shown in Figure 1.

2.1.1. Carbonization of sugarcane bagasse.

Carbonization was conducted in a vertical tube furnace. Subsequently, sugarcane bagasse was loaded on a stainless steel tubular reactor which is placed inside vertical tube furnace. The sugarcane bagasse were heated up to a carbonization temperature (400, 600, and 800°C) at a heating rate of 10°C/min and were held for about 2 hours at the carbonization temperatures under N$_2$ gas flow (20 cm$^3$/min). After this period, the products were cooled down to room temperature with nitrogen flowing into the reactor.

2.1.2. Activation of sugarcane bagasse char

10 g sugarcane bagasse chars were loaded inside the reactor situated in the furnace, and then heated up at a heating rate of 20°C/min to a carbonization temperature of 800°C under the nitrogen (N$_2$) gas flow (100 cm$^3$/min) and then the CO$_2$ gas (100 cm$^3$/min) was introduced to activate the samples for 2 hours. After activation, solid samples were cooled to room temperature under the N$_2$ gas flow. The products were kept in a desiccator for further characterization experiments.

2.1.3. Characterization of activated carbon

The determination of the porosity of activated carbon samples was carried out using N$_2$ adsorption at −196°C using surface area analyzer to assess the pore morphology of the produced activated carbon. The Brunauer–Emmett–Teller (BET) surface area, micropore and total pore volume, and pore size distribution were obtained by analyzing N$_2$ adsorption. The specific surface areas were determined
according to the BET method at the relative pressure in the range of 0.05–0.30. Pore volume was directly calculated from the volume of nitrogen held at the highest relative pressure (P/Po = 0.99). The pore size distribution (PSD) was obtained by the Barrett Joyner-Halenda (BJH) method, which was applied to the desorption branch of the isotherms. Fourier transform infrared (FT-IR) spectroscopy were conducted to characterize the surface functional groups using a Varian 3100 FT-IR Excalibur Series spectrometer. Resolution and aperture setting of 4 cm⁻¹, with a scan speed of 2.5 kHz over a wavenumber range of 4000–650 cm⁻¹ were applied to collect the spectra. An elemental analysis was carried out using by X-Ray Fluorescence. The surfaces of ACs were chemically characterized by Boehm titration and the pH zero point charge (pHZPC).

3. Results and Discussion

3.1. Yield
The activated carbon yield was defined as the final weight of product after carbonization, washing, and drying. The percent yield was determined from the relation:

\[ \text{Yield (％) } = \frac{W_c}{W_o} \times 100 \quad (1) \]

where \( W_c \) and \( W_o \) are the final activated carbon dry weight (g) and the precursor dry weight (g), respectively. The yield values of carbonized SCB chars were 32.15%, 26.12% and 20.46% for the carbonization temperature 400, 600 and 800°C, respectively. According to the results, the increase in the carbonization temperature caused a decrease in the yield values. With increasing temperature, more volatiles in samples would be released, causing a lower yield of chars. These findings are consistent with the general concept that increasing the carbonization temperature decreases the amount of the unstable volatiles on the carbon samples. The decrease in the yield for activated carbons is also justified by action of the dehydrating reagent, which provided elimination and dehydration reactions, breaking the bonds C–O–C and C–C of the raw material.

3.2. Textural characterization

Figure 2 shows the Nitrogen adsorption isotherms of activated carbons from SCB produced at different carbonization temperatures. 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 with increase in carbonization temperature. At carbonization temperature of 800°C, the Nitrogen adsorption isotherm shows an intermediate between types I and II of the referred IUPAC.
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 at temperatures 400 and 600°C 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.

Figure 2. Adsorption/desorption isotherms of N₂ at 77 K for SCB activated carbons prepared different carbonization temperatures.

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 carbonization temperatures on porosity development of activated carbon is shown in Table 1. With increase in carbonization temperatures the continual devolatilization and carbon–carbon dioxide reaction, results in the formation of fresh micropores, which increases the BET surface area and micropore volume of activated carbons. The higher BET surface area is an indication of the existence of a significant amount of microporosity. With increasing carbonization temperatures, the adsorption capacity of the activated carbon increased enhancing the amount of microporosity. At high carbonization temperatures, 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 at carbonization temperature of 800°C using activation temperature of 800°C and holding time 120 min.

**Table 1.** Characteristics of porosity in SCB activated carbons prepared different carbonization temperatures

<table>
<thead>
<tr>
<th>Carbonization temperatures (°C)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_{tot}$ (cm$^3$/g)</th>
<th>$V_{micro}$ (cm$^3$/g)</th>
<th>$D_{avg}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>225.27</td>
<td>0.1026</td>
<td>0.0636</td>
<td>4.24</td>
</tr>
<tr>
<td>600</td>
<td>405.81</td>
<td>0.1590</td>
<td>0.1177</td>
<td>3.63</td>
</tr>
<tr>
<td>800</td>
<td>661.46</td>
<td>0.2455</td>
<td>0.1989</td>
<td>2.48</td>
</tr>
</tbody>
</table>

Figure 3 illustrated the pore size distributions of activated carbons prepared at different carbonization temperatures. 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 at higher carbonization temperature had more microporous structures compared to activated carbons prepared at lower carbonization temperature.

3.3. Chemical surface characterization

Table 2 shows the elemental analyses of SCB activated carbon produced at different carbonization temperatures. Results indicate the presence of many elements with predominance of carbon in the three samples. The percentage of carbon increased after carbonization and 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 with increasing activation temperature. The increasing temperatures 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 SCB activated carbons produced at different carbonization temperatures.
<table>
<thead>
<tr>
<th>Carbonization temperature (°C)</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>H/C</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>63.42</td>
<td>0.84</td>
<td>23.47</td>
<td>0.0132</td>
<td>0.3701</td>
</tr>
<tr>
<td>600</td>
<td>69.19</td>
<td>0.41</td>
<td>15.96</td>
<td>0.0059</td>
<td>0.2307</td>
</tr>
<tr>
<td>800</td>
<td>81.38</td>
<td>0.39</td>
<td>6.04</td>
<td>0.0048</td>
<td>0.0742</td>
</tr>
</tbody>
</table>

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 at carbonization temperature of 400°C, 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 carbonization temperature increases, the total oxygen containing functional group decreases to 0.240 (600°C) and 0.196 mmol.g⁻¹ (800°C). Decrease in oxygen containing functional groups, takes mostly in the carboxylic, lactone and phenolic groups. The phenolic group decreases from 0.117 to 0.240 (600°C) and 0.196 mmol.g⁻¹ (800°C). Meanwhile the lactone group decreases from 0.117 to 0.240 (600°C) and 0.196 mmol.g⁻¹ (800°C). While the concentration of the carboxylic groups decrease from 0.117 to 0.240 (600°C) and 0.196 mmol.g⁻¹ (800°C).

Table 3. Results of the Boehm and pH_{pzc} methods for the SCB activated carbons produced at different carbonization temperatures.

<table>
<thead>
<tr>
<th>Carbonization temperature (°C)</th>
<th>Carboxylic (mmol.g⁻¹)</th>
<th>Lactonic (mmol.g⁻¹)</th>
<th>Phenolic (mmol.g⁻¹)</th>
<th>Basic (mmol.g⁻¹)</th>
<th>pH_{pzc}</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.798</td>
<td>0.017</td>
<td>1.196</td>
<td>1.963</td>
<td>5.21</td>
</tr>
<tr>
<td>600</td>
<td>0.664</td>
<td>0.012</td>
<td>1.143</td>
<td>1.635</td>
<td>5.36</td>
</tr>
<tr>
<td>800</td>
<td>0.427</td>
<td>0.011</td>
<td>0.745</td>
<td>0.867</td>
<td>5.86</td>
</tr>
</tbody>
</table>

The FTIR spectroscopy provides information on the chemical structure and functional group of SCB and its chars prepared at different carbonization temperatures, shown in Figure 4. It can be seen that the intensity of all bands present in the raw SCB declined more or less after the carbonization process. Typical infrared band assignments for SCB indicate that, SCB 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 SCB. 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 SCB could take part in the formation of hydrogen bonds. According to the four types of hydrogen-bonded structures, the pre dominant one in SCB is self-associated OH groups. The fact that the band at 3415 cm⁻¹ is somewhat broader towards lower wavenumbers suggests that SCB 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 SCB. 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 acetoxy groups (–O–COCH₃) in SCB. 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.

\[ \text{Figure 4. The FT-IR spectra of the SCB activated carbons produced at different carbonization temperatures.} \]

4. Conclusions
The carbonization temperature was determined to significantly influence the porosity of the activated carbon from SCB chars. The high carbonization temperature (800°C) generated a highly microporous carbon with a Type-I isotherm, while the low carbonization temperature (400 and 600°C) generated a mesoporous one with an intermediate between types I and II isotherm. At a higher temperature, the BET specific surface and total pore volume were higher due to enhancement of the pore development.

5. References