Utilization of Sustainable Palm Empty Fruit Bunch Sorbents for Carbon dioxide Capture

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Abstract

Sustainable porous carbons have been produced via pyrolysis of palm empty fruit bunch (EFB) and then modified using hydrogen reduction and treatment with phenol for increase in hydrophilic character. The sorbents were tested for CO₂ capture. The EFB based sorbent materials were characterized for morphology and chemical functional groups. Characterization of the porous carbons covered four samples: hydrogen reduced, hydrophilic treated, bio oil impregnated and CO₂ uptake samples. FTIR analysis showed presence of hydroxyl, carbonyl, aliphatic, esters, alcohol, phenol and carboxylic groups on the surfaces of the sorbent materials. Absence of C=O in the hydrophilic treated samples could be traced back to reaction of the phenol and compounds containing carbonyl groups. Absence of C-O stretching for ethers in the carbon captured samples could be related to oxidation of ethers in CO₂. Spectra at 557.5 cm⁻¹ could be due to adsorption of CO₂ bending stretch.

Keywords: CO₂ capture; palm empty fruit bunch; hydrophilic; pyrolysis; bio-oil substrate

1. Introduction

The control of anthropogenic CO₂ emission is a crucial matter due to assertion that CO₂ gas contribute hugely to global climate change (Servilla et al., 2011). Carbon dioxide, (CO₂) was ranked as one of the major sources of greenhouse gas emission (GHG) and directly contributes to global climate changes and human’s health (IPCC, 2007). In addition, penetration of fossil fuels in most parts of human activities which leads to CO₂ generation have aggravates this scenario. The use of sustainable solid waste material such as palm oil, pineapple wastes, rice husk and paddy straw for carbon dioxide (CO₂) capturing is a new approach to reduce excessive amount of CO₂ nowadays. Conventionally, most methods for CO₂ capture are based on different physical and chemical processes such as adsorption, absorption, membranes and cryogenics (Pirez et al., 2011; Wang et al, 2011). Application of a particular technique largely depends upon
the characteristics of the gas stream from which CO$_2$ needs to be separated, which mainly depends on the power plant technology (Jacobson, 2009). In other hands, the For process of capturing CO$_2$ emissions from power plants involves the use of toxic materials and requires 20 to 30 percent of the plant’s energy output. Consequently, the necessity for zero emission associated with green lifestyle nowadays has boosted the concerted effort to find best solution to achieve it. Due to techno-economic problems associated with the present amine system used in CO$_2$ capture, researches are devoted to find an alternative. Porous carbons are one of the leading sorbent contenders for CO$_2$ capture. Their major advantage include low cost, availability, regeneration, low energy requirement, high surface area and easily susceptible to surface and pore modifications. In this work, sustainable solid char was prepared from Empty fruit bunches (EFB) and then treated with hydrophilic phenolic solution to serve as adsorbent for CO$_2$ capture. Therefore, the aim of this paper is to study the use of reduced empty fruit bunch (EFB) as an adsorbent as well as its modification toward proper capturing of CO$_2$. Fourier transform infra-red (FTIR) technique was employed to evaluate the adsorption capacity of the porous unmodified and modified reduced EFB and the functional group effects. EFB modified can be a commercial potential source of adsorbent to replace the existing/conventional adsorbents such as amine and activated carbon thereby reducing wastes generation annually as well as improving environmental air quality.

2. Experimental

2.1 Sample Preparation

The raw empty fruit bunch (EFB) used in the experiment was obtained from palm oil plantation, Koperasi Kampung Jawi Johor Bharu Berhad. Initially, the raw EFB was dried in roller oven under temperature condition of 100°C for 24 hours, it’s then separated and stored in vacuumed desiccators. The purpose of the drying process was to remove moisture content. The solid charcoal from EFB was obtained at pyrolysis (Figure 1) temperature of 525°C±25°C, supplied with 4.5L/min N$_2$ and 1.8 psi for 3 hours. The collected products were separated into residue solid and liquids. To ensure the homogeneity in the EFB composition, the EFB was grinded to 250µm size and then used as support material for CO$_2$ capture.

![Figure 1. Schematic diagram of EFB pyrolysis batch reactor](image-url)
The sample was reduced with hydrogen gas for 3 hrs at 120mL/min±10mL/min in a batch reactor as shown in the Figure 2, then 0.4g of EFB reduction was treated in 1.4g phenolic solution as hydrophilic state, prepared by ratio 1.4g phenol to 8g water and 0.03g bio oil substrate from the pyrolysis process. The solution was left for 20 min with occasional gentle stirring 6 rpm and dehydrated in the oven evaporator for 24 hours at 100°C High-purity carbon dioxide was passed over the sample bed at a rate of 100ml/min for 3h for the uptake process of the micro porous element in the sample as in Fig. 2 and then transferred to a desiccator until use.

2.2 Characterization of Sample
2.2.1 Fourier Transform Infrared Spectroscopy (FTIR)
FTIR was used to qualitatively identify the chemical functionality of the samples. PerkinElmer FT-IR spectrometer one series model was used in the tests. The transmission spectra of the samples were recorded using KBr pellets containing 0.1% of carbon. The spectra were recorded from 4000 to 400 cm$^{-1}$. A blank test was carried out first to eliminate the buoyancy effect as described by Dantas et al. (2011).

2.2.2 Scanning Electron Microscopy (SEM)
Scanning electron microscopy (SEM) was used to observe the microstructure and the surface morphology of EFB and treated EFB chars. The instrument was a Karl Zeiss (EVO50 XVPSEM, Germany) with an acceleration voltage of 15.0 KV. The samples were coated with gold to provide about 200Å gold layer thicknesses using a vacuum sputter coater. Morphology of the samples was examined using magnification of 1000.

2.3 Carbon Dioxide Capturing
CO$_2$ adsorption studies were conducted by passing CO$_2$ gas over the adsorbents samples. The flow was maintained at 100mL/min for 3 hours at pressure of 1.6bars under ambient temperature in the range of 35°C to 65°C (Zhao et al., 2011).

3.0 Results and Discussion
3.1 FTIR
The FTIR spectra of the treated and untreated EFB derived bio-char samples are shown in Figure 2. The summary of the FTIR analysis with some probable functional groups on the samples are given in Table 1.
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Figure 2. FT-IR spectrum for bio char sieved 250µm (a) CO₂ capture (b) reduced treated hydrophilic impregnation with bio oil (c) reduced treated hydrophilic (d) pyrolysis

Table 1. FTIR functional group composition of EFB derived bio-char

<table>
<thead>
<tr>
<th>Bonding</th>
<th>Wave number(cm⁻¹)</th>
<th>Hydrophilic treated EFB impregnation with bio oil</th>
<th>CO₂ capturing EFB sample</th>
<th>Class compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H stretching</td>
<td>3600-3300</td>
<td>3400.0</td>
<td>-</td>
<td>Phenols, alcohols</td>
</tr>
<tr>
<td>C-H stretching</td>
<td>3000-2800</td>
<td>-</td>
<td>3033.9</td>
<td>Alkanes</td>
</tr>
<tr>
<td>C=O stretching</td>
<td>1750-1650</td>
<td>-</td>
<td>1717.8</td>
<td>Ketones, Aldehydes, Carboxylic acids, esters</td>
</tr>
<tr>
<td>C=C stretching</td>
<td>1675-1575</td>
<td>-</td>
<td>-</td>
<td>Alkenes</td>
</tr>
<tr>
<td>C-H stretching</td>
<td>1460-1350</td>
<td>1408.3</td>
<td>-</td>
<td>Alkanes</td>
</tr>
<tr>
<td>C-O stretching</td>
<td>1300-950</td>
<td>1223.6,1141.3</td>
<td>-</td>
<td>Primary, secondary and tertiary alcohols, phenols, ester</td>
</tr>
<tr>
<td>C-H bending</td>
<td>900-650</td>
<td>746.3</td>
<td>906</td>
<td>Aromatic compounds</td>
</tr>
<tr>
<td>CO₂ bending stretch</td>
<td>667-578</td>
<td>669.5</td>
<td>557.5</td>
<td>CO₂ bending</td>
</tr>
<tr>
<td>CO₂ stretching</td>
<td>2348</td>
<td>2368.1</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

The spectra of all the chars displayed the bands containing OH, C=C and CH stretch. This shows that they contain similar surface functional groups. However, the spectra of the samples show some differences at other points. Absence of C=O (Figure 2) in the
hydrophilic treated samples could be traced back to reaction of the phenol and compounds containing carbonyl groups. Absence of C-O stretching for ethers in the carbon captured samples could be related to oxidation of ethers in CO\textsubscript{2} (Gua et al., 2008). The spectrum of the CO\textsubscript{2} capture sample showed band at 557.5 cm\textsuperscript{-1} which could be due to the adsorption of CO\textsubscript{2} bending stretch.

3.2 Morphology of Samples
The low magnification SEM micrographs (x1000) of the surface of the porous carbon samples (Fig. 3a, b, and c) clearly showed the differences. It can be observed that raw EFB had very little pores available on the surface.

In Figure 3a, smooth surface of EFB was observed compared to Figure 3c which shows the beginning of fiber separation due to some of the lignin located in middle lamella as cement between fibers (Li et al., 2010). The separation of fiber indicates the destruction of the network of lignin, which is abundant in the middle lamella. Hence, it can probably be concluded that in the presence of bio oil and phenol in the process, brings about chemical attacks on lignin which starts an early decomposition during the impregnation process. Initially EFB (Figure 3a) input consists of a mixture of small particles and large fiber bundles. The majority of this mixture consists of large fiber bundles. The micrographs of treated EFB indicate that the large fiber bundles of EFB change to the small particles in a more uniform size with development of more cavities. As expected, the structure of fiber is disrupted during the reaction process. More uniform pores with little deposits were observed in treated and impregnated samples this could be due to carbonization (Alkhatib et al., 2011) and impregnation of bio-oil.

Conclusions
The experimental results indicated that porous carbon with well-developed porosity could be prepared from palm waste empty fruit bunches. Effect of impregnation is clearly indicated on the SEM and FTIR results. Uniform pores with little deposits on the surface were observed in treated and impregnated samples this could be due to carbonization and bio-oil addition. The spectrum of the CO\textsubscript{2} capture sample showed band at 557.5 cm\textsuperscript{-1} which could be due to the adsorption of CO\textsubscript{2} bending stretch. This indicated that EFB derived chars will be among the the alternatives CO\textsubscript{2} capture adsorbents and in gas-phase adsorption for air pollution control. Further works will be
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carried out to modify the porous carbon for enhanced selectivity towards carbon capture.

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