Pyrolysis of Palm waste for the application of direct carbon fuel cell

Shu-Hong Lim, Siek-Ting Yong, Chien-Wei Ooi, Siang-Piao Chai, Veena Doshi, Wan Ramli Wan Daud

Abstract

Direct carbon fuel cell (DCFC) is a high-temperature fuel cell which operates directly from solid carbon. From the past research, it is proven to be capable of achieving nearly 100% theoretical efficiency. Thus, DCFC commercialization would change the course of power generation industry into a more sustainable and environmental friendly means of generating electricity. Although biomass constitutes of carbon (C), they exist in different forms, making them unsuitable to be used directly as fuel in DCFC. For that purpose, heat treatment such as pyrolysis is utilized in converting the biomass into biochar which possesses slightly different physicochemical properties, such as higher C% and large surface area. It was found that, palm shell pyrolyzed at 750°C, with heating rate of 10°C/min and residence time of 1 hour produced a highly potential biochar for DCFC application.

Keywords: biochar; direct carbon fuel cell; palm shell; pyrolysis.

1. Introduction

Current electricity generation mainly depends on combustion of fossil fuels, such as coal. This method releases significant amount of pollutants into atmosphere. Such problem could be avoided with the introduction of DCFC technology. Malaysia, as the second largest palm oil exporters in the world, has...
generated ample amount of palm waste each year. Such waste could be utilized in electricity generation, presenting a sustainable yet green energy solution. However, palm wastes are similar to other biomasses; due to their undesirable physicochemical properties, they could not be used readily in DCFC. The importance of high C% in DCFC performance has been reported, such that lack of C% in the fuel could lead to linear decrease in voltage at high current density region. This is due to the restricted C consumption when large amount of electrons are flowing [1]. Additionally, presence of inorganic compounds could have catalytic or negative effects on DCFC performance [2]. Furthermore, surface oxygen functional groups could act as active sites for electrochemical oxidation; while textural properties such as extensive surface area and porosity provide extra contact between fuel and electrolyte, contributing to DCFC performance [3]. Other than the influence of constituent biomass, characteristics of biochar are highly dependent on operating conditions of pyrolysis, such as pyrolysis temperature, heating rate and residence time. It was reported that an increase in pyrolysis temperature increases C% as well as creating high surface area [4]. Moreover, long residence time and low heating rate would also promote desirable characteristics for the improvement in DCFC performance. In this study, experiment was carried out to explore the potential of using palm shell as fuel in DCFC. The effect of pyrolysis temperature on the characteristics of palm shell biochar was examined. The potential of the biochar as DCFC fuel is estimated by comparing their characteristics such as chemical composition, surface oxygen functional groups and textural properties with common DCFC fuel such as carbon black.

2. Experimental works

Palm shell was dried in the oven for 24 hours at 110°C for moisture removal. The dried palm shell was then grinded and sieved to obtain a size ranging from 0.5 mm-1 mm. 0.5 g palm shell underwent pyrolysis at 450, 600, 750 and 900°C respectively. Pyrolysis was carried out at heating rate of 10°C/min, residence time of 1 hour, and N₂ flow rate of 2 L/min. Pyrolyzed palm shell samples are denoted as PS450, PS600, PS750 and PS900 with respect to their pyrolysis temperature. Results from proximate analysis were used in the selecting biochar of high similarities with carbon black in terms of chemical composition. The selected biochar were further examined in terms of surface area, porosity and functional groups through N₂ adsorption, and Fourier transforms infrared spectroscopy (FTIR), respectively.

3. Results and discussion

Table 1 Proximate analysis of biochar samples and carbon black.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Moisture</th>
<th>Volatile matter</th>
<th>Fixed carbon</th>
<th>Ash content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Black</td>
<td>2</td>
<td>0</td>
<td>94</td>
<td>4</td>
</tr>
<tr>
<td>PS450</td>
<td>5</td>
<td>29</td>
<td>63</td>
<td>3</td>
</tr>
<tr>
<td>PS600</td>
<td>4</td>
<td>11</td>
<td>81</td>
<td>4</td>
</tr>
<tr>
<td>PS750</td>
<td>4</td>
<td>6</td>
<td>86</td>
<td>4</td>
</tr>
<tr>
<td>PS900</td>
<td>5</td>
<td>3</td>
<td>87</td>
<td>5</td>
</tr>
</tbody>
</table>

As shown in Table 1, the volatile matter, C% and ash content increase with increasing pyrolysis temperature. However, the increment is non-linear and stays rather constant after 750°C. It was reported that a high concentration of volatiles will be released during pyrolysis at high temperature and part of the volatiles could be trapped within the carbon matrix of biomass, forming secondary char that contributes to a high C% [4]. Beyond thermal treatment at 750°C, the release of volatiles and C formation are almost completed, and resulting in consistency in chemical composition of biochar samples. By comparing PS450 to the rest of biochar samples and carbon black, it is evident that the release of volatiles is
incomplete, and the C% may be too low to be used as DCFC fuel. As for PS600, the volatile content is rather high. In terms of chemical composition, PS750 and PS900 have higher degree of similarity with that of carbon black, making them highly potential as DCFC fuel. Thus, PS750 and PS900 were selected for further characterization.

Table 2 Surface areas, volumes, and average pore size of biochar and carbon black by N₂ adsorption analysis.

<table>
<thead>
<tr>
<th>Samples</th>
<th>S_{BET} (m²/g)</th>
<th>V_{total} (cm³/g)</th>
<th>S_{micro} (m²/g)</th>
<th>V_{micro} (cm³/g)</th>
<th>D_{average} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Black</td>
<td>202.99</td>
<td>0.39</td>
<td>137.38</td>
<td>0.07</td>
<td>7.90</td>
</tr>
<tr>
<td>PS750</td>
<td>204.31</td>
<td>0.10</td>
<td>203.04</td>
<td>0.10</td>
<td>1.95</td>
</tr>
<tr>
<td>PS900</td>
<td>270.88</td>
<td>0.13</td>
<td>255.60</td>
<td>0.13</td>
<td>1.85</td>
</tr>
</tbody>
</table>

As shown in Table 2, PS750 and PS900 possessed higher surface area as compared to carbon black. Surface area increases with increasing pyrolysis temperature. As observed in Figure 1, the adsorption isotherms of PS750 and PS900 belong to Type I isotherm, suggesting adsorption occurs on microporous solids, this result is in conjunction with the micropore structure of biochar, which contributes to most of the total surface area. However, with the increase in relative pressure, a slight decrease in quantity of N₂ adsorbed is observed. This situation could be due to the insufficient energy possessed by N₂ for adsorption. CO₂ adsorption will produce a more accurate measurement [5]. As for carbon black, it exhibits Type III isotherm, which suggests the structure is non-porous. Furthermore, the average pore diameter of carbon black is 7.90 nm and this confirmed the lack of micropores in carbon black. The higher surface area of biochar samples is believed to be able to compensate for the lack of fixed carbon as compared to carbon black. Higher surface area enables more contact between fuel particles and anode layer, enabling higher electrochemical oxidation rate of carbon in DCFC.

Fig. 2. Adsorption isotherms of (a) carbon black, (b) PS750 and (c) PS900.

As shown in Table 2, PS750 and PS 900 possessed higher surface area as compared to carbon black. Surface area increases with increasing pyrolysis temperature. As observed in Figure 1, the adsorption isotherms of PS750 and PS900 belong to Type I isotherm, suggesting adsorption occurs on microporous solids, this result is in conjunction with the micropore structure of biochar, which contributes to most of the total surface area. However, with the increase in relative pressure, a slight decrease in quantity of N₂ adsorbed is observed. This situation could be due to the insufficient energy possessed by N₂ for adsorption. CO₂ adsorption will produce a more accurate measurement [5]. As for carbon black, it exhibits Type III isotherm, which suggests the structure is non-porous. Furthermore, the average pore diameter of carbon black is 7.90 nm and this confirmed the lack of micropores in carbon black. The higher surface area of biochar samples is believed to be able to compensate for the lack of fixed carbon as compared to carbon black. Higher surface area enables more contact between fuel particles and anode layer, enabling higher electrochemical oxidation rate of carbon in DCFC.

Fig. 2. FTIR spectra of carbon black and biochar samples PS750 and PS900.
As shown in Figure 2, it is evident that all three curves are of highly similarity, suggesting the presence of similar functional groups. Band at 3400 cm\(^{-1}\) corresponds to O-H stretching due to presence of H\(_2\)O, phenol or alcohol groups. Band at 2900 cm\(^{-1}\) is associated with C-H stretching of aromatics. Band at 1600 cm\(^{-1}\) is associated with C=C stretching of aromatic compounds. Bands at 1400 cm\(^{-1}\) and 1100 cm\(^{-1}\) correspond to O-H bending of alcohol or carboxylic acid and C-O stretching of alcohol, respectively. A band at 2260 cm\(^{-1}\) corresponds to nitrile group, can be observed for carbon black and PS750. The absence of nitrile group in PS900 could be due to high thermal treatment on the biochar, which possibly causes thermal degradation of the nitrile group [6]. The high similarities in terms of presence of oxygen-based functional groups in both carbon black and biochar samples further elevate the potential of biochar as DCFC fuel. These oxygen functional groups provide active sites for carbon oxidation in DCFC.

4. Conclusion

Palm shell biochar produced by pyrolysis at temperature beyond 750 °C exhibit high similarities in term of chemical composition. Furthermore, biochar obtained at 900 °C possesses much larger surface area as compared to carbon black. Both biochar and carbon black contain similar oxygen functional groups. These similarities give an indication that palm shell biochar could be a highly potential fuel for DCFC. Nevertheless, reaction testing of biochar in DCFC is recommended to give a quantitative measurement of its suitability. Furthermore, additional characteristics such as morphology and degree of graphitization should be examined for in depth comparison with carbon black.

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References


Biography

Dr. Sick-Ting Yong obtained her Ph.D. degree in Chemical Engineering from the National University of Singapore. She is a lecturer in Monash University Sunway Campus, Malaysia. Her research interests include the synthesis of nanostructured materials, fuel processing for fuel cell applications, direct carbon fuel cell, catalytic reaction and membrane separation.