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PAPER • OPEN ACCESS

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To cite this article: N Jafri *et al* 2020 *IOP Conf. Ser.: Earth Environ. Sci.* **463** 012061

View the article online for updates and enhancements.

Utilization of mesocarp fiber and the impact of its physicochemical properties on the performance of direct carbon fuel cells

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Abstract. Direct carbon fuel cell (DCFC) is a promising technology for power generation. It works on the utilization of solid carbon fuel and is high in efficiency with low emissions. In this study, biochar derived from oil palm mesocarp fibre (PMF) biomass was evaluated as a fuel supply in a DCFC based on solid-oxide electrolyte. To understand the connection between the physicochemical properties and electrochemical performance of PMF biochar (carbon fuel) in DCFCs better, the PMF biomass is subjected to acid and alkali pre-treatment for structural modification. All samples are characterized by means of thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET) and scanning electron microscope (SEM) tests to obtain the link between cell performance and fuel characteristics. The maximum power density of pre-treated PMF biochars reached up to 40-55% level when compared to conventional fuels. In specific, the HCl-treated PMF biochar showed the highest electrochemical reactivity in the DCFC, giving a maximum power output of 11.8 mW cm^{-2} at 850 °C. It is found that after pre-treatment, the thermal stability of the biochar increases along with an increase in the surface area and pore volumes. Henceforth, these factors are believed to have a pronounced impact on the electrochemical reaction in the DCFC.

1. Introduction

Fuel cells generate electrical energy at high efficiency and are categorized based on the fuels they oxidize, such as hydrogen, methanol and methane. The configuration and theoretical principles of the direct carbon fuel cell (DCFC) are similar to that of solid oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC) which also run on high temperature [1,2]. DCFCs utilize solid carbonaceous substrates, such as coal, carbon black, activated carbon, graphite, or biomass-based biochars. The DCFC efficiency (cumulative product of theoretical, voltage and fuel utilization efficiencies) is about 80%. The general system efficiencies have been estimated to be above 60-70% which is inclusive of system auxiliary losses [3]. The DCFC broadly falls into three categories depending on the functioning electrolyte namely molten carbonate, molten hydroxide or solid ceramic electrolyte [4]. The most serious problems associated with molten carbonate and molten hydroxide cells are electrolyte stability, degradation and leakage due to the corrosive nature of the electrolyte [4-6]. On the contrary, solid ceramic electrolyte based DCFCs which are all-solid-state devices, do not suffer from issues characteristic to molten electrolyte DCFCs.

Malaysia stands second globally in the production of palm oil and the production generates massive amounts of waste biomass. One-third of this waste comes from palm mesocarp fibre (PMF), palm kernel shell (PKS) and empty fruit bunch (EFB), while the other two-third comes from oil palm frond (OPF) and oil palm trunk (OPT) through the oil extraction process [7]. PMF biomass contains a relatively high amount of lignin which translates into solid biochar. A high char content means a high carbon value, indicative of the carbonaceous nature of the biomass [8]. This property makes the resulting biochars a strong reactive fuel in the DCFC system as carbon is the main substrate for electrochemical reactions in DCFCs [9,10]. Higher content of fixed carbon also corresponds to more chemical energy, i.e. a high calorific value, thus leading to a better DCFC performance [11]. With DCFC utilizing solid carbon to generate electricity, this creates opportunity to make use of the potential of PMF biochar as carbon fuel. However, the electrochemical performance of carbon fuels at the anode is one of the major hindrances of application in the DCFC. Hence, different surface treatment methods such as alkali, acid, heat, laser, and plasma treatments, are typically used on the carbon fuels to improve their electrochemical performance [12].

Therefore, the objective of this study is to examine the possibility of utilizing pre-treated PMF biochar for DCFC application. The study also aims to explore the correlation between the physicochemical properties of the pre-treated PMF biochar through surface modification and their electrochemical performances in the DCFC system. A comparative analysis of the electrochemical performance between PMF biochar and commercial activated carbon (AC) fuel in the DCFC system is also outlined. The significance of this research lies in demonstrating the potential of waste PMF biomass as an alternative fuel source in the DCFC. The importance of the research also lies in making DCFC technology a sustainable and cleaner alternative to conventional power generation approaches.

2. Experimental

Waste biomass from palm mesocarp fiber (PMF) was collected from an oil palm plant in Sri Ulu Langat in Dengkil, Selangor, Malaysia. The three kinds of biomass used in the study were PMF biomass pre-treated with HCl, PMF biomass pre-treated with NaOH and untreated PMF, herein referred to as 'PMF-HCl', 'PMF-NaOH' and 'U-PMF', respectively. Commercial activated carbon (AC) was procured from Sigma Aldrich (M) Sdn Bhd Malaysia. Acid and alkaline pre-treatment with 2 M of HCl and 3 M of NaOH respectively were conducted on PMF biomass [12,13]. Pre-treated PMF biomass was then dried in the oven (UN75, Memmert, USA) according to the ASTM D2867-09 method of drying at 105 ℃ for 24 h. The pre-treated PMF biomass samples were subjected to pyrolysis in a horizontal split quartz tube (HST 12/400, Carbolite) in an atmosphere of 99.9% N_2 flowing at 1 L min^{-1}. The heating was done at 10 ℃ min^{-1} to a final temperature of 500 ℃. The samples were maintained at 500 ℃ for 1 h and were then subsequently cooled and stored. The thermal decomposition of biochars was examined on thermogravimetric analyzer (TGA) (STA 6000, Perkin Elmer thermo-balance, USA). 10 mg of samples were heated from 30 ℃ to 900 ℃ in a nitrogen atmosphere at a heating rate of 10 ℃ min^{-1}. At 900 ℃, inert gas supply was cut off and replaced with oxygen gas at a flow rate and heating rate of 20 ml min^{-1} and 10 ℃ min^{-1}, respectively. The samples were held at this stage for 20 mins for ash determination [14]. Surface area of the selected biochar samples were determined by Brunauer-Emmett-Teller (BET) analysis using Autosorb 1C (Quantachrome Instruments, USA. Scanning electron microscope (SEM) (Hitachi S3400N-II, Japan) was employed to examine the surface morphology. The DCFC performance test of the biochars at different operating temperatures was conducted by placing 0.1 g of the sample on the button cell. The button cell was positioned between the anode and cathode ceramic tubes and comprised of a cathode (LSM), anode (Ni-YSZ), and electrolyte (YSZ) purchased from Ningbo SOFCMAN Energy Technology Co. Ltd., China. Silver wire was used for current collection and carried high conductivity. The anode side was supplied with N_2 gas at a constant flow rate of 600 ml min^{-1} and the cathode side was supplied O_2 gas at a constant flow rate of 200 ml min^{-1} from portable cylinders. Upon reaching the respective targeted temperatures of 750 ℃, 800 ℃ and

850 ℃, the voltage output (referred to as open-circuit voltage, OCV) was measured. All electrochemical assessments were done using a Potentiostat (Gamry, Interface 1000E, Germany). The electrochemical tests were started after the OCV reached a steady state. The current-voltage (*I-V*) curve of the run was evaluated with a scan rate of 10 mV s^{-1} and an excitation voltage amplitude of 30 mV. The data was recorded for all the biochar samples.

3. Results and discussion

Figure 3.2 shows the weight loss curves for the raw, untreated and pre-treated biochars using TGA tests under nitrogen environment. For raw PMF biomass and untreated PMF biochar, the start of oxidation begins around 300 °C, which is lower than that of PMF-HCl and PMF-NaOH. Hence, the thermal stability is considered to decrease in the order PMF-HCl > PMF-NaOH > U-PMF > Raw PMF. As anticipated, there was less moisture and volatile matter in the pre-treated biochars compared to the raw PMF biomass and untreated PMF biochar both of which decomposed actively. The analysis of the raw PMF biomass and untreated PMF biochar shows the thermal decomposition at temperatures of 300 °C and above which is due to the release of volatile matter. The weight loss of PMF biochars was observed between 400 °C to 700 °C due to minor thermal decomposition. This outcome indicates the effect of thermal decomposition in biochars to be limited, hence suggesting that the carbon in the biochar exists mostly in the solid state. At the temperature of 700–850 °C, there were only less than 10% of weight loss which indicates that carbon in the biochar can take part in the overall electrochemical reaction in the DCFC [15].
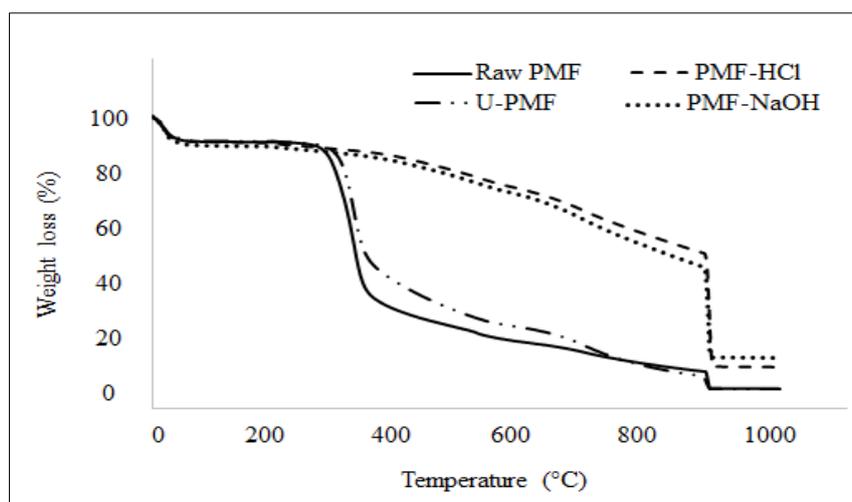

Figure 3.1: TGA curve for raw PMF biomass and PMF biochars.

The surface area is a significant property which is related to the physical interaction area between the electrolyte and carbon particles. The surface area and total pore volumes of all the fuels were estimated by BET method (Table 3.1). The recorded values of the biochars were higher than the raw PMF biomass. The BET specific surface area of PMF raw biomass was 0.310 m^2 g^{-1} which increased to 412.330 m^2 g^{-1} and 378.050 m^2 g^{-1} for HCl and NaOH treated biochar, respectively. The high value of BET surface area and pore volume of pre-treated biochars is probably associated with the pre-treatment conditions which disrupted the biomass fibre structure and resulted in the formation of pores, thus increasing the total surface area. The pore size evaluations are also significant for the reactivity of the biochar which helps in improving the anodic reaction by increasing the contact area between the carbon particles and oxide ions [16].

Treatment with HCl and NaOH changes the range of porosity in the raw PMF biomass along with increasing the diameter of the pores from 2-10 µm to 2-60 µm noticed through SEM analysis. This may lead to the generation of additional active sites in the carbon fuel for the electrochemical oxidation reaction. Meanwhile, the surface area of the untreated PMF biochar was recorded lower at 342.042 m^2 g^{-1}.

Table 3.1: BET analysis of the biochars.

Biomass sample	BET surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})
AC	805	0.452
Raw PMF	0.310	0.001
U-PMF	342.042	0.154
PMF-NaOH	378.050	0.960
PMF-HCl	412.330	0.980

Figure 3.2 displays SEM images of the raw and pre-treated PMF biochars. Figure 3.2(a) shows raw PMF biomass whose surface is covered with small particles. After pre-treatment of raw PMF biomass with dilute HCl and NaOH, there was leaching of particles and the biochar surface looked disrupted. The leached particles from the raw PMF biomass by pre-treatment might be minerals and extractives [17,18]. As reported, pre-treatment led to the partial dissolution of mineral components and hemicellulose which resulted in enhanced surface areas and pore volumes [19]. Overall, pre-treatment partially damaged the biomass framework, though the primary structure was unaltered. Pre-treatment also led to increase in the range of porosity in the biochars along with increasing the diameter of the pores from 2-10 µm to 2-60 µm. This probably generated new active sites in the carbon fuel for the electrochemical oxidation reaction.
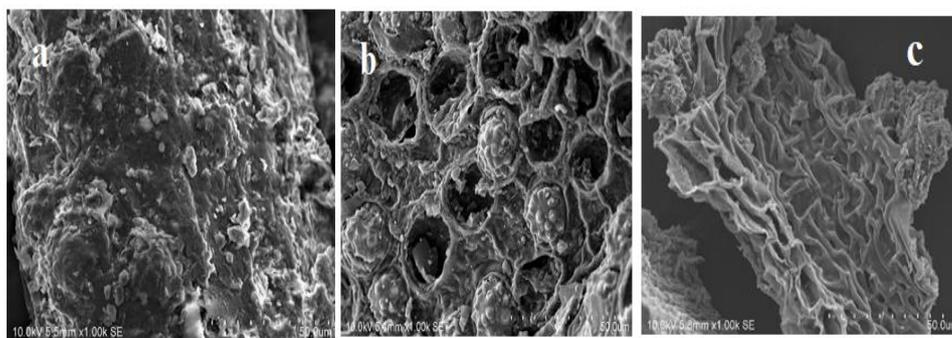

Figure 3.2: SEM micrographs of (a) raw PMF biomass (b) HCl treated PMF biochar (c) NaOH treated PMF biochar.

DCFC testing was performed using AC fuel, pre-treated and untreated PMF biochars. Figure 3.3(a) and 3.3(b) displays the polarization curve of HCl treated and NaOH treated PMF biochars, respectively. The biochars were assessed for their electrochemical performance at 750 °C, 800 °C & 850 °C and the results are shown in Figure. 3.3(a) and Figure. 3.3(b). The experimental results of open circuit voltage (OCV) for all the carbon fuels were recorded and comparisons made. It is seen that HCl and NaOH treated PMF biochars gave slightly higher values of OCVs, current and power densities in comparison to untreated PMF biochars and AC fuel as shown in Table 3.2. The polarization curves shown for the HCl and NaOH treated PMF biochars in Figure 3.3 are similar in shape and the samples show a similar electrochemical pattern.

The curves decline from peak voltage of 0.89 V to nearly 0.2 V. The best performance is obtained by HCl treated PMF biochar sample which exhibits a maximum power density of 3.2, 5.7 and 11.8 mW cm^{-2} at 750 °C, 800 °C and 850 °C, respectively. In a DCFC system which runs on a solid ceramic electrolyte, the electrochemical oxidation reaction takes place within a constrained reactive area where there is a direct contact between the carbon particles, electrode and the electrolyte. Consequently, the structure and surface area of the carbon fuels influence the current and power density values [20,21]. It is likely that the surface area and pore volume of the carbon fuels are strongly linked to the probability of better interaction with the electrolyte, which positively impacts the electrochemical discharge frequency of carbon fuels. From the BET results shown in Table 3.1, the surface area and pore volume of the HCl treated PMF biochar was recorded at a value of 419.365 m^2 g^{-1} and 0.960 cm^3 g^{-1}, respectively. The high BET surface area and pore volume of the biochar are favourable for anodic reactions. Weaver et al. [22] reported that a higher surface area positively influences the working of DCFCs. Likewise, Li et al. [12] stated that a higher surface area and higher pore volumes improve interaction with the electrolyte. The SEM results of HCl treated PMF biochar showed the biochars to consist of broader pores (pore size >0.1 mm) which means that a relatively increased surface of carbon particles could come in good contact with the electrolyte surface. This also probably contributed towards their better performance in the DCFC.
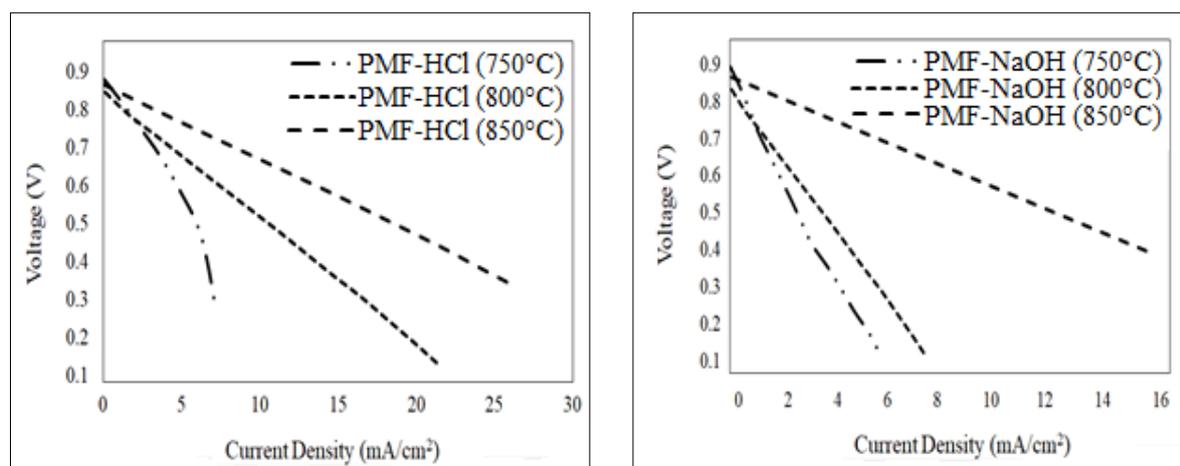

Figure 3.3: *I-V* curve of DCFC operated on (a) HCl and (b) NaOH treated PMF biochar fuel at 750 °C, 800 °C & 850 °C.

Table 3.2: Electrochemical data for biochar fuels at 850 °C.

Carbon fuels	Open circuit voltage (V)	Current density (mA cm^{-2})	Power density (mW cm^{-2})
AC	0.79	10.2	4.2
U-PMF	0.78	7.8	3.5
PMF-HCl	0.89	27.1	11.8
PMF-NaOH	0.87	15.3	4.8

4. Conclusion

Oil palm based PMF biomass was pre-treated with HCl and NaOH for structural modification. Subsequently, the association between the physicochemical properties and electrochemical performance of the PMF biochar in the DCFC was examined. The significant changes in the physicochemical properties of the HCl and NaOH treated PMF biochars included higher thermal stability, high surface area and increased pore volumes which led to the enhancement in the electrochemical reactivity of PMF biochars in the DCFC. The best results were obtained by HCl treated PMF biochar which gave an OCV of 0.89 V and maximum power density of 11.8 mW cm^{-2} at 850 °C. The results, therefore, support that the carbon fuel structure plays an essential part in DCFC performance. Hence, structural alteration of carbon fuels may prove to be a practical approach to enhance the application of fuels in DCFC systems.

Acknowledgement

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