

EFFECT OF ALKALINE PRE-TREATMENT ON RICE HUSK-DERIVED BIOCHAR FOR DIRECT CARBON FUEL CELL

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Abstract

A variety of agricultural wastes such as corn cob, coconut shell and oil palm empty fruit bunch are produced every year. Biomass which undergo pre-treatment could be used to produce biochar with various applications such as direct carbon fuel cell (DCFC) as a renewable energy source. Rice husk was selected in this study as the high lignin content in rice husk in this biomass has would produce biochar with higher carbon yield. This research aims to study the effect of alkaline pre-treatment on biochar production for DCFC. Initially, rice husk was pre-treated by using NaOH with a concentration of 0.4 M at 60 °C for 24 h. Subsequently, the pre-treated sample and together with untreated sample which serves as control was pyrolysed at 500 °C. DCFC performance was studied on both alkaline pre-treated and untreated biochar at different operating temperature (550 °C, 650 °C, and 750 °C). This study revealed that the open circuit potential of biochar with alkaline pre-treated showed a higher value of 845 mV as compared to the untreated sample with 807 mV. Thus, pre-treated sample producing a higher power density of 44.6 μWcm^{-2} . Interestingly, the specific surface area of the pre-treated sample showed the BET surface area of pre-treated rice husk-derived biochar was found to be lower than untreated rice husk-derived biochar indicating that surface area is not the sole factor that influence the DCFC performance. The lower ash content and higher carbon content in the biochar shown to be a more prominent factor affecting on the DCFC performance. In summary, it was concluded that alkaline pre-treatment on biomass showed the ability to improve the biochar's properties which facilitates DCFC performance.

Keywords: Rice husk, Biochar, Pyrolysis, Direct carbon fuel cell, Alkaline treatment.

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Abbreviations

AFC	Alkaline Fuel Cell
BET	Brunauer Emmett Teller
DCFC	Direct Carbon Fuel Cell
DMFC	Direct Methanol Fuel Cell
FTIR	Fourier Transform Infra Red
MCFC	Molten Carbonate Fuel Cell
OCP	Open Circuit Potential
PAFC	Phosphoric Acid Fuel Cell
PEMFC	Polymer Electrolyte Membrane Fuel Cell
SOFC	Solid Oxide Fuel Cell
TGA	Thermogravimetric Analysis

1. Introduction

Fuel cell, typically made with the assembly of membrane-electrodes, is an electrochemical device that converts chemical energy of a fuel into electrical energy [1]. The difference between fuel cell and battery is that the fuel cell can continue to function whenever the fuel is supplied while a battery's life is dependent solely on the capacity of the energy storage within itself. There are many types of fuel cells, differentiated by the types of electrodes, electrolytes and operating temperatures. These include, polymer electrolyte membrane fuel cell (PEMFC), alkaline fuel cell (AFC), direct methanol fuel cell (DMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), solid oxide fuel cell (SOFC) and direct carbon fuel cell (DCFC) [2]. High temperature fuel cells (range between 600 °C to 1000 °C) such as SOFC, MCFC and DCFC draw great interest among researchers owing to its higher electrical efficiency than low temperature fuel cells. Interestingly, direct carbon fuel cell can produce higher electrical efficiency of 70 – 90 % compared to the other two aforementioned fuel cells, having less than 65 % electrical efficiency. In addition, DCFC that uses carbon as the fuel showed to be a potential fuel cell technology used in countries with vast agricultural activities such as Malaysia. With the need of solid carbon solely as direct fuel without further gasification, biomass is foreseen to be a potential renewable carbon source [3].

DCFC can be further distinguished by the type of electrolytes, such as, molten hydroxide, molten carbonate and oxygen ion conducting ceramic. As for the oxygen ion conducting ceramic electrolyte, it can be further classified on its carbon delivery mechanism, such as solid carbon, carbon mixed with molten metal and carbon mixed with molten salt [2]. The disadvantage of DCFC with molten carbonate or molten hydroxide electrolytes is the electrolyte degradation and the risk of liquid leakages during the operation. Whilst, for the oxygen ion conducting ceramic electrolyte, there is no volatilisation of the electrolyte and risk of liquid leakages [4]. In addition, carbon mixed with molten metal, such as tin, increases the anodic polarisation losses due to the use of porous ceramic separator. Another disadvantage of fuel delivery system via molten carbonate is, it increases the corrosion of nickel anode and other cell components. It further reduces the stability in 8YSZ electrolyte with the formation of lithium zirconate in the presence of Li/K carbonate eutectic mixture at 700 °C [2]. Whereas, with solid carbon fuel, it produces carbon monoxide and carbon dioxide and provides the highest power density. Thus, DCFC with oxygen ion conducting ceramic

electrolyte and solid carbon fuel is foreseen to be the best configuration of DCFC [2, 4].

Nonetheless, DCFC possesses a drawback of rapid corrosion and degradation on its membrane-electrodes components [5, 6]. Many research has been conducted by using coal, proposed that the presence of impurities affects the efficiency of the DCFC system [7, 8] and the system durability is affected consequently. Thus, ash free carbon sources are required for this technology. Therefore, pre-treatment of biomass sources either, chemical treatment, mechanical treatment, heat treatment or by combination of any need to be experimented.

It has been suggested that the use of biomass char are comparatively produces a better efficiency than the fossil fuels, in which, fossil fuels may not environmentally friendly [9 - 11]. Biomass primarily composes of three main constituents in its cell wall, namely, hemicellulose, lignin and cellulose. During the biochar production via charring process, hemi-cellulose will be decomposed first and followed by decomposition of cellulose and lignin [12, 13]. Aliphatic carbon in biomass is converted to fused-ring aromatic carbon during charring process and it further lose its volatilisation. Lignin consists of aromatic carbon compared to cellulose and hemi-cellulose, hence biomass with higher lignin content will decompose slower and contribute to a higher carbon yield [14].

Rice husk consist of 34.4 % of cellulose, 29.3 % of hemicellulose and 19.2 % of lignin [15]. While, empty fruit bunch is having 20.4 % lignin content [16] and oil palm fiber is within 13.2 % to 25.3 % [17]. With the high lignin content found in palm oil based biomass, several researchers [18] have paid attention on its potential as carbon fuel in energy production in this region and have shown a positive energy production outcome. However, it would be interesting to reveal the potential of other types of biomass with sufficiently high lignin content in the similar application and thus rice husk is chosen in this study.

Recent study in the DCFC technology proposed the possible characteristic of the carbon fuel for an enhanced performance. One of the factors that affects the performance is the chemical composition of the fuel itself. High percentage of fixed carbon improved the cell performance [19, 20]. In contrast, the presence of the higher ash content, which also may contain SiO_2 and Al_2O_3 , lowered the cell performance [19, 21]. In addition, the textural properties are highlighted. These includes the pore sizes, surface area and the particle size of the carbon fuel source. The presence of the mesoporous carbon structure contributes to a better electrolyte transfer. It was also supported that, higher surface area aids in the anodic reaction as the better contact between the electrolyte and the carbon fuel [22, 23].

A study was conducted with the raw coal and coal treated with nitric acid showed decreased in ash content and sulphur content. This further contributed to a better fuel cell performance [24]. In another study, the anode surface was further analysed by EDX after the DCFC performance and it shows that the presence of Al and Si were deposited on the anode surface and for the long term durability of the DCFC operation is affected [25]. To further support on the inhibitive effect on anode reaction, the impurities such as SiO_2 and Al_2O_3 was shown to decrease the current density to 14 and 15 mA/cm^2 at 0.9 V. In addition of the catalytic minerals such as Fe_2O_3 , Na_2O , K_2O , MgO and CaO during the performance of DCFC, it resulted to a much higher current density at 0.9 V [19].

In a study conducted by Markovska et al. [26] for silica extraction and Johar et al. [16] for cellulose fiber and nanocrystal extraction shows that the NaOH treatment on rice husk can effectively remove silica, one of the main constituent in rice husk ash.



This will further contribute for a reduce ash content in rice husk biochar for its further application in DCFC. However, lack of study for this pre-treatment method on biomass for DCFC application.

Besides the factor of biochar properties in DCFC performance, the operating parameter such as temperature of DCFC do affect its performance. An increase on operating temperature of DCFC, it increases the open-circuit potential value [25]. Application of the corn cob biochar in direct carbon fuel cell produces 1.05 V with the power density of 185 mW cm⁻² at the temperature of 750 °C [27].

Hence, this study will be focused on the effect of alkali pre-treated rice husk on the performance of the DCFC. Besides that, the effect of biochar properties and the operating temperature of DCFC will be investigated further for a better DCFC performance.

2. Methodology

2.1. Materials

Rice husk was collected from Oblique Titi Rice Mill Co., Inc., Perak, Malaysia. NaOH, 99.9 % was provided by Friedemann Schmidt Chemical, Malaysia.

2.2. Preparation of biochar

2.2.1. Pre-treatment of rice husk

Rice husk was washed with distilled water to remove the soil and other present contaminants. Subsequently, it was placed into an oven (UN75, Memmert, USA) at 105 °C for 24 h for moisture removal (ASTM D2867-09) [28]. Upon drying, rice husk was grinded by using grinder (JK-SG-160, KGC Scientific) and sieved into particle size of 0.5-2.0 mm using a sieve shaker (RX-812-1, Tyler). The rice husk powder produced was kept in a desiccator prior to the usage. Pre-treatment were carried out on 15 g of rice husk in 150 ml of 0.4 M NaOH solution under stirring condition at temperature of 60 °C for 4 h [17] with a hotplate stirrer (IKAC-MAG HS 7S2, Aplab Saintifik). The pre-treated rice husk was further washed until pH 7. Pre-treated rice husk powder was then dried again in the oven (UN75, Memmert, USA) following the same ASTM D2867-09 standard at 105 °C for 24 h for moisture removal [26].

2.2.2. Pyrolysis

A laboratory scale pyrolysis reactor was used to pyrolyse pre-treated rice husk. A conventional tube furnace (HST 12/400, Carbolite) with a quartz tube of 1 m length by 0.08 m internal diameter was used. Two alumina crucibles were used to

hold the rice husk powders [29]. The rice husk was pyrolysed with a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ to temperature of $500\text{ }^{\circ}\text{C}$ and held for 1 h [15, 29, 30]. Pyrolysis was carried out in a non-oxidative atmosphere with nitrogen gas flowed at 1 L min^{-1} . Nitrogen was introduced into the pyrolysis reactor 10 min before the commencement of heating to purge the furnace tube. The biochar produced was collected after cooling.

2.3. Characterisation of biochar

2.3.1. Physicochemical characterisation

The pre-treated and untreated biochar were characterised on its physicochemical properties. CHNS elemental composition analyser (Elementar vario MACRO Cube) was used to determine the elemental composition of biochar, following the combustion method and Dumas method (standard method). Specific surface area of biochar was analysed using Brunauer–Emmett–Teller (BET) analysis on Quantasorb SI Instrument (Quantachrome, USA). Briefly, around 0.285 g of biochar derived was degassed at $300\text{ }^{\circ}\text{C}$ for 5 h prior to N_2 adsorption measurement at 77 K [31]. On the other hand, proximate analysis of biochar was conducted using thermogravimetric analyser (STA 6000, Perkin Elmer) in a non-oxidative atmosphere under pure nitrogen environment with nitrogen flow rate of 0.05 L min^{-1} . The biochar was heated from room temperature to $800\text{ }^{\circ}\text{C}$ at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ [32]. The changes in the surface functional groups of biochar after pre-treatment was analysed on Fourier transform infra-red (FTIR) spectroscopy (Spectrum, 100, Perkin Elmer) measured from 4000 cm^{-1} to 400 cm^{-1} by KBr method.

2.3.2. Electrochemical characterisation

Figure 1 shows the set up for the DCFC stack for electrochemical tests. Silver wire was used as current collector. Button cell was placed in between the anode and cathode alumina tube. The button cell comprises of anode (Ni-YSZ), cathode (LSM) and electrolyte (YSZ). Both anode and cathode alumina tube will be connected by using mechanical compression. Gas inlet on top of anode was fed with nitrogen flowed at 600 ml min^{-1} and cathode was fed with purified air. Prior of heating, anode was purged with nitrogen to remove any residual gas residue in the chamber. Upon reaching the targeted temperature, polarisation curves and open circuit potential (OCP) were measured at the scan rate of 1 mV s^{-1} on a potentiostat (Gamry, Interface 1000E). The internal resistance was tested at high frequency of 1 kHz [19, 33]. Biochar loading in the DCFC was 0.1 g. Both treated and un-treated biochar samples were tested for the DCFC performance at the temperature of $550\text{ }^{\circ}\text{C}$, $650\text{ }^{\circ}\text{C}$ and $750\text{ }^{\circ}\text{C}$.

3. Results and Discussion

3.1. Weight loss of biomass

Table 1 shows the weight loss of pre-treated and untreated biochar derived from rice husk before and after NaOH treatment and pyrolysis. For NaOH treatment of rice husk, there were four runs to ensure repeatability of the study. The four runs

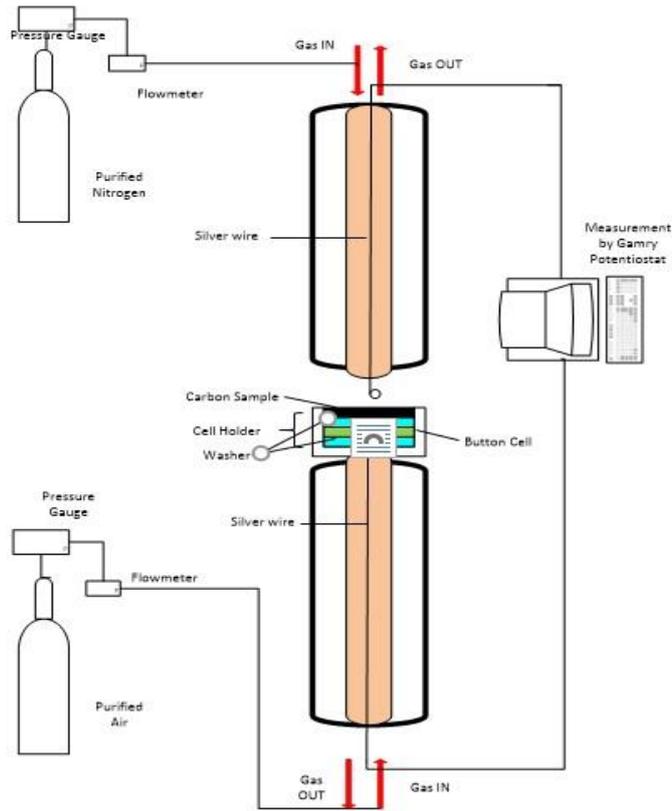


Fig. 1. Set up of DCFC stack.

showed that the rice husk decreased to around 10-11 g from 15 g after the NaOH treatment which was approximately 74.52 % of solid yield. This was in good agreement with the study done by McKay et al. [17] that the same NaOH treatment condition had achieved a solid yield of 79 %. After the pre-treated rice husk undergone pyrolysis process, the biochar yield was found to be 35.52 % which is slightly lower than 39.49 % biochar yield of untreated rice husk. The biochar yield of untreated rice husk after pyrolysis, 39.49 % was in good agreement with the study of Windeatt et al. [29] that the rice husk had biochar yield of 39.00 %.

Table 1. Weight loss of pre-treated and untreated biochar derived from rice husk before and after NaOH treatment and pyrolysis.

	Weight, g (Untreated)	Weight, g (Pre- treated)
NaOH Treatment	-	15.01
Before Pyrolysis	15.00	11.18
Solid Yield (%)	-	74.52
After Pyrolysis	5.92	3.97
Biochar Yield (%)	39.49	35.52

Table 2 displays the biochar yields from different biomasses. It can be observed that untreated rice husk has the highest biochar yield compared to other types of biomass. Although the pre-treated rice husk has slightly lower biochar yield of 35.52 %, it is only surpassed by cotton stalk with biochar yield of 38.00 %. However, biochar with higher carbon content yield remain the main objective for biochar production as biochar yield was just a gravimetric indicator [34].

Table 2. Comparison of biochar yield of different biomass [29].

Biomass	Biochar Yield (%)
Palm Shell	31.8
Sugarcane Bagasse	27.7
Coconut Shell	28.2
Wheat Straw	30.3
Cotton Stalk	38.0
Olive Pomace	30.5
Coconut Fibre	30.8
Untreated Rice Husk (Literature)	39.0
Untreated Rice Husk (This study)	39.5
Pre-treated Rice Husk (This study)	35.5

3.2. Elemental composition analysis

The results of elemental composition analysis in Table 3 shows that the carbon composition of biochar derived from rice husk increased from 55.61 % to 70.63 % after the NaOH pre-treatment. There is an increase in hydrogen composition in the pre-treated rice husk biochar. The results were aligned with previous study [17, 26] that the composition of carbon and hydrogen increased after the NaOH pretreatment. In this study, it was found that alkaline treatment able to increase the carbon content in the biochar which might improve the DCFC performance.

It was observed that the composition of nitrogen and sulphur decreased after the NaOH pre-treatment. High sulphur content could cause permanent degradation of Ni-YSZ cermet via bulk sulphidation. This is because sulphur can easily react with nickel, forming nickel sulphide with lower thermal stability [35]. It has been proven by Cherepy et al. [36] that sulphidation decreased DCFC performance via the decrease of carbon discharging rate and the increase of cell resistance.

Table 3. Elemental composition analysis of pre-treated and untreated biochar derived from rice husk.

	Untreated	Pre-treated
Carbon (%)	55.617	70.632
Hydrogen (%)	2.879	3.384
Nitrogen (%)	2.613	1.752
Sulphur (%)	0.042	0.035

3.3. BET surface area analysis

It is observed from Table 4 that the surface area of the biochar derived from rice husk was the lowest compared to other biochar or carbons. Biochar derived from rice husk was having the closest surface area to biochar derived from almond

shell and graphitic carbon. Li et al. [22] had showed that graphitic carbon has lower open circuit potential compared to carbon black or activated carbon which have higher surface area. In contrast, a study by Elleuch et al. [37] on biochar derived from almond shell has shown that the open circuit potential was still relatively high, which was around 1.0-1.1 V regardless of its low surface area. Comparing the surface area of untreated and pre-treated biochar derived from rice husk, it was found that the untreated biochar had higher surface area compared to pre-treated biochar. NaOH treatment should increase surface area of biochar as the ash was removed from the structure of the biochar however our experimental results showed a lower value which possibly attributed to the simultaneous decomposition of biochar with ash. This is because the decomposed organic matter may have blocked the pores, causing pre-treated biochar to have a lower surface area [38].

Table 4. BET surface area analysis of pre-treated and untreated biochar derived from rice husk compared with literature results.

Biochar	BET Surface Area (m^2g^{-1})	References
Wood-chips	544	[39]
Charcoal	729	[39]
Carbo medicinalis	1249	[39]
Graphitic Carbon	39	[22]
Carbon Black	118	[22]
Activated Carbon	1241	[22]
Almond Shell	30.35	[37]
Untreated Rice Husk	21.30	This study
Pre-treated Rice Husk	11.05	This study

3.4. Thermogravimetric analysis (TGA)

Two main stages of mass release could be observed in Fig. 2. The first stage was referring to the release of moisture from room temperature to at around 150 °C [26]. It could be seen that the pre-treated biochar derived from rice husk had only 1.979 % of moisture, which was lower than the moisture of untreated biochar derived from rice husk around 5.078 %. This might be due to the removal of hemicellulose and cellulose which is more hydrophilic compared to hydrophobic lignin during NaOH pre-treatment together with ash. This resulted to moisture in pre-treated biochar is easily released during drying process after NaOH pre-treatment [40].

The second stage was the release of volatile matters at around 300-700 °C in which the main structure of biochar derived from rice husk was disrupted during this stage. [26, 37, 41]. It was shown that pre-treated biochar derived from rice husk has only 14.92 % of solid residue. The presence of the volatile matter and moisture may lower the DCFC performance. This finding is supported by a study conducted by Chien et al. [33] concluding that the presence of volatile matter and moisture content reduced the calorific value in pine charcoal and thus leading, to a poor DCFC performance. Hence, it can be further validated that pre-treatment of biomass before subjecting to DCFC is important as the reduced moisture and volatile matter would improve the DCFC performance.

During second stage, untreated biochar derived from rice husk had a lower weight loss rate compared to pre-treated biochar. The pre-treated biochar started to decompose around 378.94 °C while the untreated biochar derived from rice husk started to decompose only around 431.54 °C. This phenomenon may be caused by the presence of high ash content in untreated biochar derived from rice husk which caused a barrier to prevent the decomposition of biochar [33]. It might also be due to a higher hemicellulose and cellulose content of the untreated biochar. Hemicellulose and cellulose decomposed within 200-400 °C, however, due to the high hemicellulose and cellulose content in untreated biochar, the lignin structure decomposed at the higher temperature of 431.54 °C compared to the pre-treated biochar [32]. Similar findings were obtained by Markovska et al. [26]. It also observed from Fig. 2 that the pre-treated biochar derived from rice husk had been destructed completely before 800 °C.

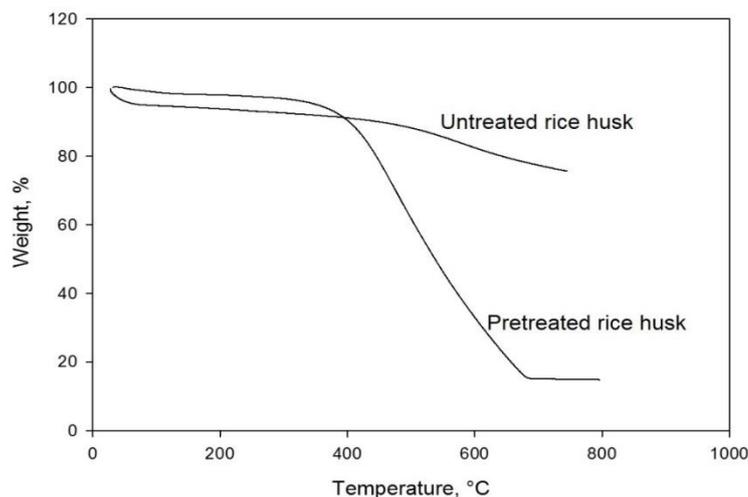


Fig. 2. Thermogravimetric analysis (TGA) of pre-treated and untreated biochar derived from rice husk.

3.5. FTIR Characterisation

The functional groups of the biochar samples were analysed by using FTIR spectra and the results obtained is shown in Fig. 3. Broader bands were observed at the region of 3600 – 3000 cm^{-1} which can be attributed to hydroxyl groups (-OH). It was observed the presence of band at 495 cm^{-1} in untreated rice husk biochar might be contributed by Si-H group [42]. The same peak was not being detected in NaOH pre-treated sample. This confirms the removal of silica and impurities during NaOH pre-treatment. A few peaks were observed at the range of 1071 cm^{-1} with higher intensity in pre-treated biochar, shows the C-O stretching which referring to ether, alcohol or phenol structures. Higher peak intensity was observed in pre-treated samples and vibration stretching peaks at 1607 cm^{-1} represent the C=O groups. The oxygen functional group which present at the surface atoms or resides in alkyl chains aids in a better Boudouard reactivity [43] which facilitates DCFC performance.

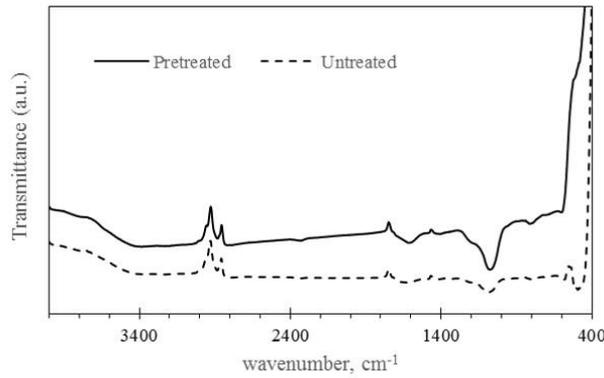


Fig. 3. FTIR spectra for pretreated and untreated rice husk char.

3.6. Open circuit potential (OCP)

Figure 4 displays the graph of OCP against temperature for both pre-treated and untreated biochar derived from rice husk. It was observed that OCP increased as the temperature increased for both samples. Higher OCP value of 0.845 mV were observed at 750 °C for pre-treated samples. This suggests that the reactivity of the electrodes sites increased with higher temperature and thus enhancing the anodic reaction kinetics [37]. In addition, a lower OCP was observed for untreated biochar samples may be attributed by lower ions presences at the electrode site for a better reactivity [21].

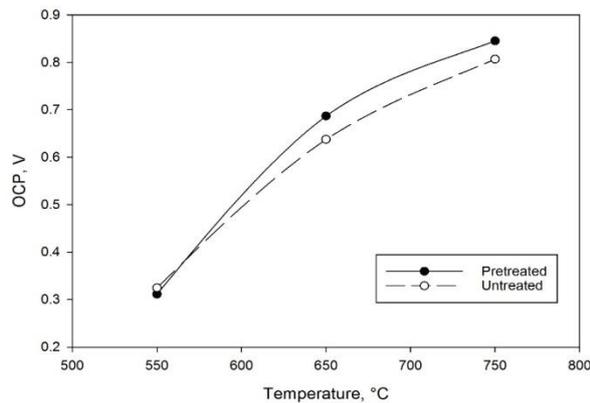


Fig. 4. OCP of pre-treated and untreated biochar derived from rice husk at temperature of 550 °C, 650 °C and 750 °C.

The trend of pre-treated rice husk OCP over the time at different temperature is illustrated in Fig. 5. At 750 °C, OCP was found to gradually reduced over time when it is higher than 0.8 V Whilst, at the temperature of 650 °C and 550 °C, the voltage increased steadily over time. These results suggest that at the temperature of 750 °C, the carbon in the samples are being consumed via the anodic reaction, leaving only ashes behind on the button cells. At 550 °C, a low voltage is shown as no activation in between the button cell and the carbonaceous sample [44]. In addition, as the temperature of the fuel cell increases, a better electrochemical

oxidation occurs. Thus, during the reaction, the possible reverse Boudouard reaction occurs and produces CO:



So, it suggests that, the reverse Boudouard reaction does not occur at lower temperature [45]. In another study, it shows that, energy and fuel losses happen due to the fuel consumption when CO used as the fuel source in the fuel cell. Hence, the Boudouard reaction does not contribute to a better electrochemical activity [46, 47]. However, a different trend was observed for the untreated samples as shown in Fig. 6. OCP value at both temperature of 750 °C and 650 °C remained stable over the investigated period. On the contrary, the OCP reading at 550 °C were noticeably high in the beginning and it reduced over time. This result might be due to the improper contact in between the cell and the current collector. The treated samples behave differently with a better and more efficient electrochemical reaction compared to untreated samples as the latter only obtained 0.63 V at the start of the measurement compared to 0.84 V when pre-treated sample was used at 750 °C. It can also be seen that after 300 s for pre-treated 750 °C graph, the OCP reading is reaching the stable value. This can be due to the fuel consumption over the time and the reaction is reaching the equilibrium.

Table 5 displays a summary on the physical and electrochemical characteristic of pre-treated and untreated biochar derived from rice husk together with other carbon fuels at 750 °C. It could be observed that activated carbon had the highest BET surface area and the highest OCP of 1.34 V compared to carbon black and graphitic carbon. Corn cob and almond shell biochar had similar OCP to graphitic carbon which they may be graphitic considering the BET surface areas and OCP. Biochar derived from rice husk had the lowest OCP compared to other biochar and carbon fuels and this is explainable with the lowest surface area and volatile matter content. However, the OCP was around 60-70 % of carbon black which means that it still has the potential to be used as fuel in DCFC. Interestingly, a higher OCP was obtained from pre-treated biochar with lower surface area and lower ash content compared to untreated biochar. The OCP results of pre-treated and untreated biochar indicates that the BET surface area may not be a significant factor affecting OCP value as compared to ash content.

Further examination was performed on the pore volume and pore diameter of biochar. Studies have been reported that anodic reaction was generally improved with high surface area or pore volume of biochar due to the better contact in between biochar and anode [22]. While another study with coal suggested that surface area alone is not sufficient to produce higher electrochemical reaction. The porosity of the fuel plays major role in allowing a better diffusion of the ions during the reaction. When the biochar has mesoporous structure, it will have a higher pore mean diameter [48]. This study shows that pre-treated rice husk biochar is more mesoporous compared to untreated rice husk biochar, which suggest a good correlation with the power density obtained. Significant improvement in the power density was observed with pre-treated biochar. Thus, rice husk has been shown as one of the prominent carbon fuel in DCFC due to its higher pore mean diameter despite having a lower surface area. However, the obtained power density value is still far lower than the reported literature which uses molten carbonate salt as the additive to the carbon produced. This might be

due to the lower contact of solid carbon fuel and anode which results in a higher resistance to power production.

The DCFC performance showed that the NaOH pre-treated rice husk provided higher electrochemical activity compared to untreated rice husk. The maximum output at 750 °C were $44.6 \mu\text{Wcm}^{-2}$ and $1.79 \mu\text{Wcm}^{-2}$, respectively for pre-treated and untreated samples (Table 6). For both pre-treated and untreated samples, the current density increases with the decrease of the voltage. This is due to the limitation of carbon oxidation rate during the fuel cell performance [33]. Study by Li et al. [49], shows that the deposited carbon at the three-phase boundary and at YSZ and Ni particles provides a better electrochemical reaction. From a study by Nabae et al. the maximum output at 700 °C was $6.4 \mu\text{Wcm}^{-2}$ and $1.2 \mu\text{Wcm}^{-2}$ at 550 °C [45]. The lower power density obtained in this study could be improved by increasing the contact of carbon fuel with anode site of DCFC. Another possible reason for a lower power density can be due to the ohmic resistance that occurs when temperature is below 800 °C [50]. The ohmic resistance can be overcome by reducing the thickness of the electrolyte [50]. Besides that, the difficulty of fuel diffusion with oxidants at the interface of current collector and electrode might also lead to lower power density. Continuous carbon feed during DCFC operation might improve the power density [33].

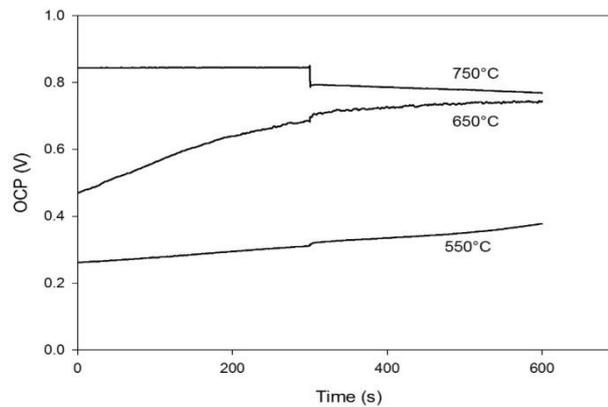


Fig. 5. OCP of pre-treated biochar derived from rice husk against time.

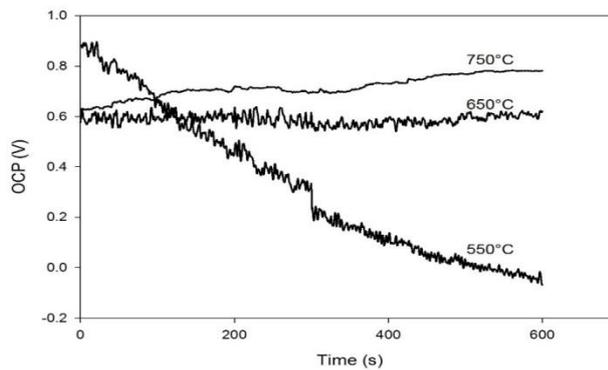


Fig. 6. OCP of untreated biochar derived from rice husk against time.

Table 5. Electrochemical performance of pre-treated and untreated biochar derived from rice husk compared to other carbon fuels at 750 °C.

Carbon Fuel	BET Surface Area (m ² g ⁻¹)	Volatile Matter (%)	OCP (V)	References
Graphitic Carbon	39.00	96.00	1.05	[22]
Carbon Black	118.00	96.00	1.26	[22]
Activated Carbon	1241.00	93.00	1.34	[22]
Corn Cob Biochar	-	92.02	1.05	[27]
Almond Shell Biochar	30.35	90.50	1.03	[37]
Untreated Rice Husk Biochar	21.30	-	0.81	This study
Pre-treated Rice Husk Biochar	11.05	80.01	0.85	This study

Table 6. Comparison on surface area, pore volume and pore diameter of different biochar and its power density.

Fuels	S _{BET} (m ² g ⁻¹)	V _{Total} (m ³ g ⁻¹)	D _{Pore} (Å)	Power Density	Reference
Untreated rice husk biochar	21.2965	0.046297	51.068	1.79 μWcm ⁻² @ 0.4V	This Study
Pre-treated rice husk biochar	11.0523	0.018623	98.393	44.6 μWcm ⁻² @ 0.41V	This Study
Shenhua coal	6.1183	0.005088	80.152	49.7 mWcm ⁻²	[48]
Shenhua char	162.9957	0.086632	3.7281	35.02 mWcm ⁻²	[48]
Adaro coal	0.7968	0.002409	159.327	67.89 mWcm ⁻²	[48]
Adaro char	212.2973	0.118518	4.2899	51.06 mWcm ⁻²	[48]

4. Conclusion

From the study conducted, pre-treated rice husk biochar is proven to give better electrochemical activity compared to the untreated rice husk biochar. The improvement in DCFC performance might be attributed to the higher percentage of carbon and hydrogen with lower ash content in pre-treated biochar derived from rice husk compared to untreated biochar. The higher amount of surface oxygen functional group obtained after alkaline pre-treatment also improves the electrochemical activity.

On the other hand, it was found that higher OCP contributed by better anode and solid fuel contact might not be solely dependent on BET surface area, but also on pore volume and pore diameter. The potential of utilising rice husk as biochar in

DCFC is promising when the OCP of biochar derived from rice husk was found to be approximately 60-70 % of the OCP obtained from carbon black. The most suitable DCFC temperature is found at 750 °C, which produces power density of 44.6 μWcm^{-2} and 1.79 μWcm^{-2} from treated and untreated samples respectively.

For future study, the operating conditions of pyrolysis and NaOH treatment can be further optimised to produce biochar with relatively higher biochar solid yield and carbon content. Further efforts in improving the power density from biomass-derived biochar in DCFC operation is deemed necessary to improve the economic feasibility of this green technology in electricity generation.

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