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To cite this article: L K Palniandy *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **268** 012124

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Comparison of woody and non-woody biomass as a fuel source for direct carbon fuel cell

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Abstract. Direct carbon fuel cell (DCFC) is an emerging technology for energy production. The application of biomass in DCFC will be a major transition from the use of coals to generate energy. However, the relationship between biomass or biochar composition and electrochemical performance of DCFC is yet to be studied. The performance of DCFC by using carbon fuel originated from woody and non-woody biomass were compared and investigated in this study. The effect of pyrolysis temperature ranges from 550 °C to 850 °C on the preparation of biochar from rubberwood (RW) and rice husk (RH) was evaluated for power generation. However, the presence of high ash content of more than 30% in RH biochar reduced the cell performance compared to RW biochar with only less than 10%. The presence of impurities such as silica in RH biochar are detrimental for cell performance, and this might be a factor for the production of lower power density (0.07 mW/cm²) compared to a higher power density (0.5 mW/cm²) obtained from RW biochar. The presence of oxygen functional group on the surface of RW biochar might have aided its higher electrochemical performance. This study concludes that woody biochar fuels are feasible for DCFC application, and further optimization of DCFC could be investigated.

1. Introduction

Fuel cell technologies have recently attracted great attention owing to its advantage to produce clean energy using renewable energy sources [1]. These technologies use simple electrochemical process to convert chemical energy into electrical energy. They differ themselves from the fossil fuel energy generation, which requires a complex conversion from heat energy to mechanical energy and to electrical energy with lower efficiency that is limited by the Carnot efficiency [2]. Several types of fuel cells have been investigated targeted for different applications. In view of the utilisation of biomass energy, direct carbon fuel cell (DCFC) has shown its potential as energy generation device using carbon fuel at high temperature operation. The success of this system can benefit the chemical industry in which waste heat energy can be integrated into the DCFC system to generate extra energy



on-site. With a proper design of the DCFC system, it possesses the highest electrical efficiency of 70 – 90 % among all types of fuel cells.

At the current state, commercial carbon black and coals have been studied as the DCFC carbon fuel for energy generation with high energy efficiency obtained [3, 4]. Nonetheless, these carbon sources are non-renewable and hence they do not contribute to the carbon neutral cycle. Recent efforts have focused on searching renewable carbon sources from biomass as the more sustainable fuels. Several works have investigated on using different types of biomasses to produce biochar as fuel source for DCFC. Literatures show that the maximum power density achieved by different biochar were ranged from 12 to 185 mW/cm², with the system operated at temperature ranged between 700 to 800 °C [5]. It can be observed that biomass categorised as woody-type such as almond shell [6], olive wood [7], Acacia wood chips [8] and etc have shown to possess relatively high power density of near to 100 mW/cm² and above as compared to non-woody biomass, which only produce power density of approximately 30 mW/cm² and below. Among the many factors would affect the energy production in the DCFC system, it can be seen that the type of fuel source plays a vital role. The conversion of biomass into biochar using pyrolysis would alter the chemical composition of the fuel source and retaining most high energy value carbon content [9]. For example, the carbon content of rubber wood biochar is approximately 97.3% [10] as compared to the raw rubber wood with carbon content of only 43.98 % [11]. The presence of impurities and different functional groups in the biochar was believed to affect the DCFC performance as well [12, 13]. It is believed that the differences in the chemical composition between woody and non-woody biomass has led to a major difference in the DCFC power density obtained.

Therefore, this study aims to compare the effect of using biochars derived from woody (rubber wood) and non-woody biomass (rice husk) on the DCFC performance. The relationship between the structure and composition of biochar and performance of DCFC will be revealed to understand the major factors that promote and demote the DCFC performance.

2. Materials and methods

2.1. Pyrolysis of biomass

The collected rice husk and rubber wood biomass were washed by using distilled water. Then, it is dried in oven at 110 °C for 24 hours. The dried biomass was grinded and sieved into particle size smaller than 500 µm. The proximate analysis of raw RW and raw RH was carried out by using Thermogravimetric Analyser (TGA8000, Perkin Elmer). The pyrolysis process was conducted by using horizontal split tube furnace (Carbolite, HST 1200) under nitrogen feed flow of 150 ml/min. The pyrolysis temperature at 550 °C, 650 °C, 750 °C and 850 °C with the heating rate of 10 °C/min for 60 min were applied. All the samples were labelled as RW for rubber wood (RW550, RW650, RW750 and RW850) and RH for rice husk (RH550, RH650, RH750 and RH850) respectively.

2.2. DCFC Performance

The DCFC setup used in this study were the same as employed in previous study [14]. Button cell were placed on the sample holder and solid biochar were loaded on the anode. The biochar loading in this study was 100 mg per run. Silver wire was used as current collector at both anode and cathode. Both anode and cathode chamber were compressed mechanically. Nitrogen flows through the anode at 200 ml/min, whereas air flows through cathode at 200 ml/min. The DCFC system was heated to 850 °C at the heating rate of 10 °C/min. The electrochemical performance was studied by using potentiostat (Interface 1000E, Gamry Instrument). Upon reaching the target temperature, open circuit potential (OCP) test were measured at the scan rate of 1 mV/s by using a potentiostat (Gamry, Interface 1000E). The internal resistance was tested at high frequency of 1 kHz [15].

2.3. Biochar Fuel Characterization

Biochar derived from rice husk and rubber wood were further subjected for characterization. Proximate analysis of the rubber wood and rice husk biochar was carried out using a Thermogravimetric Analyzer (TGA800, Perkin Elmer). The heating was carried out from room temperature to 110 °C under nitrogen gas flow and was hold for 20 minutes. Then, the temperature

was ramp from 110 °C to 950 °C and was hold for 20 minutes. Gas were switched to air flow at 950 °C and were hold for another 20 minutes [16]. The presence of surface functional group of biochar was analysed by using the Fourier transform infrared (FTIR) (Spectrum100, Perkin Elmer) transmission analysis. The samples were analysed by using the attenuated total reflection (ATR) accessory from 4000 cm⁻¹ to 650 cm⁻¹ at resolution of 4 cm⁻¹ [17].

3. Results & Discussion

3.1. Effect of pyrolysis temperature on the biochar characteristic

Table 1 and Figure 1 represent the proximate analysis and weight loss of the biochar from different biomass sources in this study. The first mass loss observed at the temperature below than 100 °C for all samples in Figure 1 was due to the removal of water. An increasing trend in percentage of moisture was observed with the increase of pyrolysis temperature. The higher moisture content might be due to the hygroscopic characteristic of biochar pyrolysed at higher temperature, reabsorbing moisture from the surrounding [18]. The pyrolyzed biochar for both rice husk and rubber wood shows a significant decrease in volatile matter and increase in fixed carbon content with pyrolysis temperature increases. The production of volatile matter is due to the breakdown of carbohydrate fraction at higher temperature [19]. Rubber wood biochar contains a higher fixed carbon content compared to rice husk in general. This might be attributed to the higher lignin and cellulose contents in raw rubber wood compared to rice husk. A maximum carbon content of 67.0% was obtained from RW as compared to only 43.4% from RH. Rubber wood derived biochar shows decrease in ash content with an increased in pyrolysis temperature. This might be attributed by the volatilization of inorganic compounds into gas or liquids at higher pyrolysis temperature [20]. However, high ash content was observed in all rice husk derived biochar which may be contributed by the presence of silica in the raw biomass. From the Figure 1, it is observed that the thermal stability of pyrolyzed biochar increases compared to the raw biomass.

Table 1. Proximate analysis of biomass carbon fuel.

Type of Biochar	Moisture (%)	Volatile Matter (%)	Fixed Carbon (%)	Ash (%)
RH550	3.5	40.9	19.5	36.1
RH650	5.2	18.2	41.6	35.1
RH750	6.7	12.9	42.7	37.7
RH850	7.3	11.9	43.4	37.4
RW550	7.5	23.8	62.0	6.7
RW650	8.1	22.4	67.0	2.5
RW750	10.8	24.0	62.7	2.4
RW850	14.2	21.8	62.0	2.1

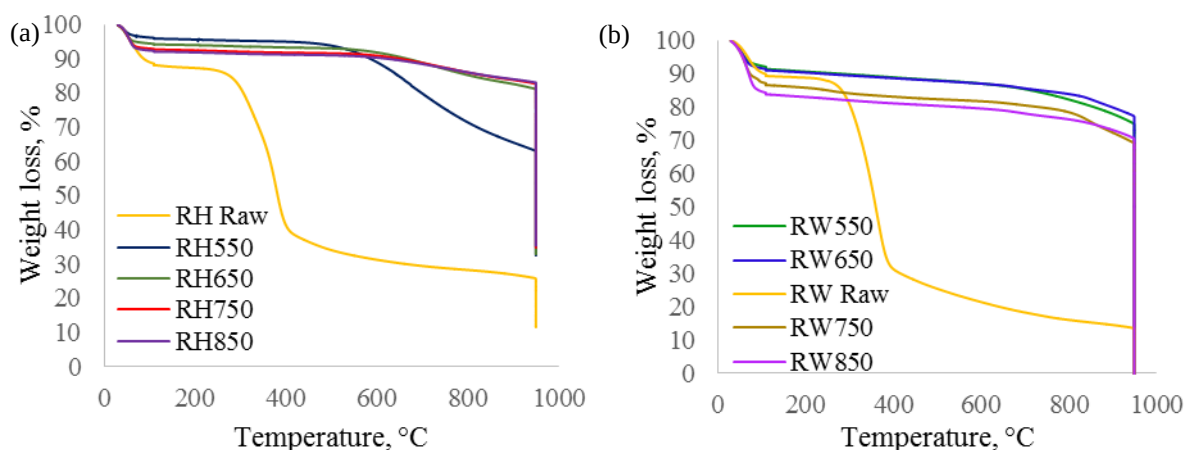


Figure 1. Thermogravimetric analyser curves for (a) rice husk derived biochar (b) rubber wood derived biochar.

FTIR analysis allows the detection of the functional group in biochar prepared at different pyrolysis temperature. Figure 2 (a) and (b) shows the spectra for rubber wood biochar and rice husk biochar respectively. A peak was observed at 1570 cm^{-1} for RW550, and it was broadened after increments in pyrolysis temperature as shown by the peak with the highest intensity for RW850. It represents the aromatic C=C and C=O stretching of conjugated ketones and quinones, which suggests the presence of phenolic and carboxylic compound in lignin is increasing with an increase of pyrolysis temperature [20]. The peaks in the range of 1269 cm^{-1} to 1020 cm^{-1} (symmetric C=O stretching that presence in cellulose, hemicellulose and lignin) [21] of RW550, decomposes further after an increase in pyrolysis temperature. This shows that the volatile matter starts to decompose after pyrolysis temperature of $550\text{ }^{\circ}\text{C}$ and a broadened peak at 1030 cm^{-1} which possibly shows the trait of C-C-O asymmetric stretch was formed [17]. The formation of peak at the range of $3000\text{--}2900\text{ cm}^{-1}$ after the pyrolysis temperature of $650\text{ }^{\circ}\text{C}$ for rubber wood biochar shows the presence of aliphatic C-H groups. In addition, new peak formed at approximately 1800 cm^{-1} (ester group) after of the biomass was pyrolysed at $550\text{ }^{\circ}\text{C}$. This attributed to the interaction between cellulose and lignin during the heating of the rubber wood samples [22]. The changes of the bands at the region of $1000\text{--}1400\text{ cm}^{-1}$ shows the band for C-O, the oxygen-containing functional groups whereas O-H stretching vibration are represented at the range of $3000\text{--}3445\text{ cm}^{-1}$ [23]. These peaks decreased in intensity with the increase in pyrolysis temperature. The phenomenon might be caused by the increased moisture content in biochar produced at higher pyrolysis temperature. This activity may be resulted from the cracking and reforming reactions of aromatic hydrocarbon in the biochar [24]. Rubber wood biochar has possessed a higher amount of surface oxygen functional group compared to the rice husk.

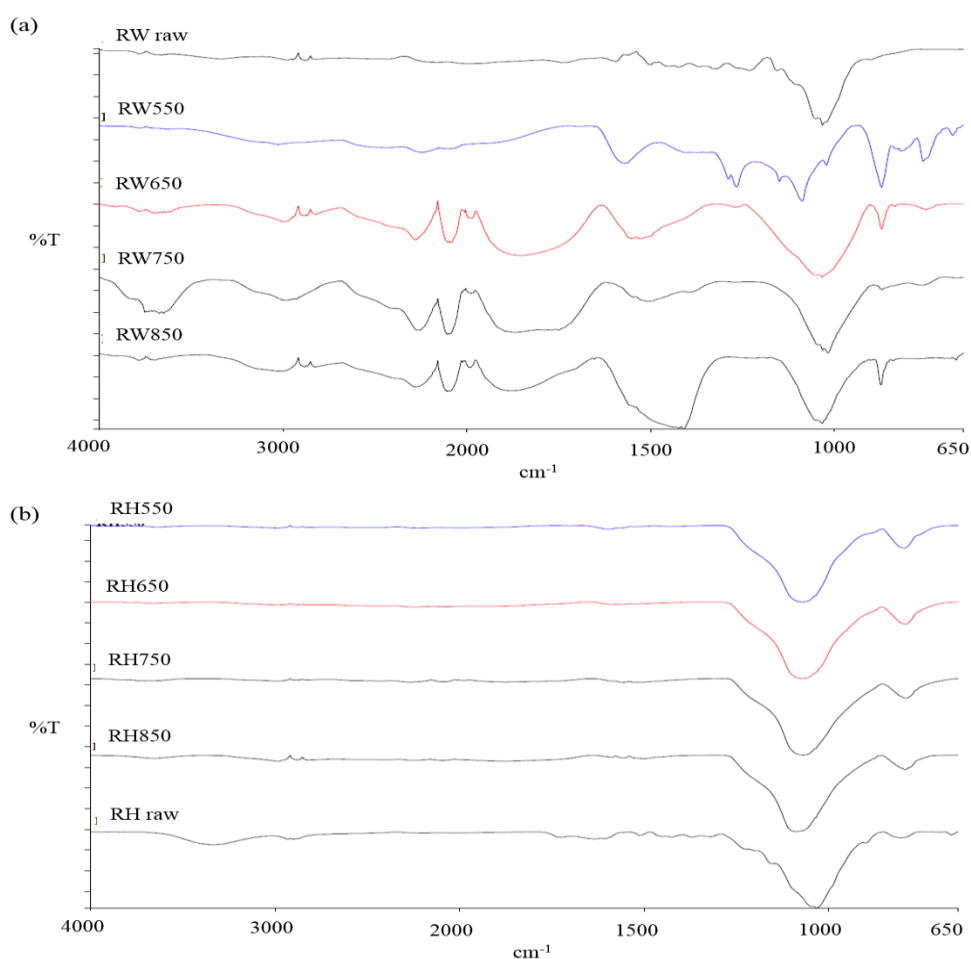


Figure 2. FTIR spectra for (a) rubber wood derived biochar, (b) rice husk derived biochar

3.2 DCFC performance test with direct solid fuel

DCFC performance test were carried by applying the solid carbonaceous fuel directly onto the button cell of the DCFC. Figure 3 (a) and (b) shows the polarization curve of both rice husk and rubber wood biochar samples from various pyrolysis temperature. From the figures, a rapid fall in the OCP for all rice husk derived biochar and RW750 might be attributed by the activation resistance as observed in other studies using activated carbon as the solid fuel [4]. However, a fast decrease with unstable potential change at higher current density might shows that the fuel consumption is faster than it is supplied to the electrode which refers to the mass transport limitation [4]. By referring to the maximum power density as shown Table 2, rubber wood biochar showed to possess higher electrochemical activity ($0.12 - 0.57 \text{ mW cm}^{-2}$) than rice husk biochar ($0.05 - 0.07 \text{ mW cm}^{-2}$), disregard to the pyrolysis temperature in biochar preparation. This indicates that woody biomass possess better electrochemical oxidation ability compared to non woody biochar. The relatively low power density and quick potential drop observed in rice husk biochar could be attributed to the high ash content (ca. 36-37 %). It was believed that the ash that is mainly from silica content acted as a barrier for the carbon to be in contact with the anode surface and thus severely block the active sites of the anode for oxidation [15]. In contrast, lower ash content in woody biochar contributes a better electrochemical activity with the maximum reported power density value of 0.57 mW cm^{-2} at RW850. In addition, the higher composition of fixed carbon in rubber wood biochar samples could also possibly contribute to the better performance due to a better fuel utilisation per active surface area. Rubber wood pyrolysed at 850°C shows a slightly higher reactivity with the highest power density. However, all the rubber wood pyrolysed at different temperature shows a similarity in the maximum

output of the DCFC cell, exception on RW750 which shows a lower performance, which requires further investigation.

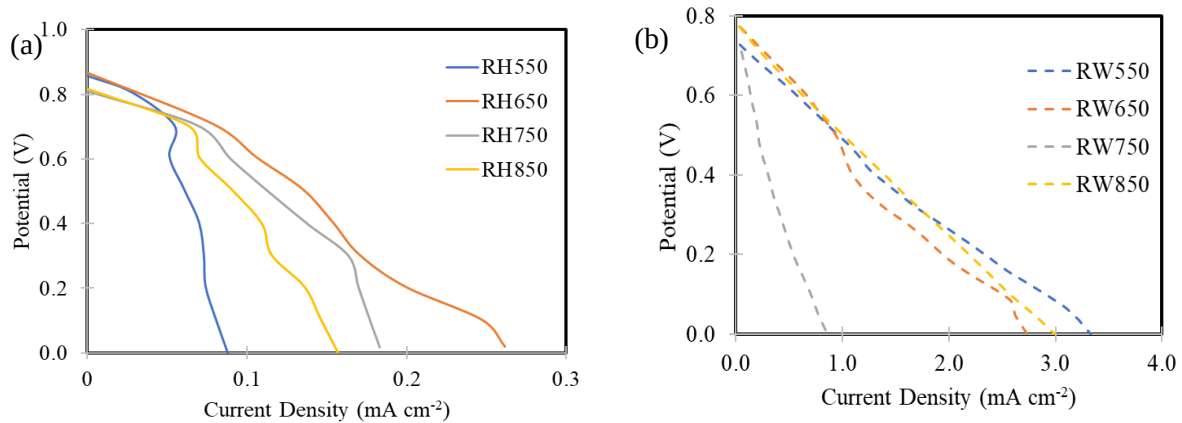


Figure 3. Polarization curve of (a) rice husk derived (a) biochar, (b) rubber wood derived biochar studied in DCFC at 850 °C.

Table 2. Electrochemical data for rubber wood and rice husk derived biochar studied in DCFC at 850 °C.

Parameter	RW550	RW650	RW750	RW850	RH550	RH650	RH750	RH850
OCP (V)	0.73	0.77	0.71	0.77	0.86	0.86	0.81	0.81
i at 0.7 V (mA cm^{-2})	0.14	0.29	0.06	0.27	0.05	0.08	0.07	0.06
i at 0.4 V (mA cm^{-2})	1.32	1.05	0.35	1.40	0.07	0.16	0.14	0.11
i at 0.1 V (mA cm^{-2})	2.91	2.51	0.71	2.57	0.08	0.25	0.18	0.14
$P_{\max}$ (mW cm^{-2})	0.55	0.49	0.12	0.57	0.05	0.07	0.06	0.05

4. Conclusion

Biochar derived from rubber wood is suitable to be applied for direct carbon fuel cell for alternative in energy production. Rubber wood biochar produces higher power density compared to rice husk biochar. High power density is correlated to the higher fixed carbon content and the presence of oxygen functional groups in rubber wood biochar which aids in electrochemical activity of DCFC. However, the presence of high ash content in rice husk contributed by the high silica content in the biomass has negatively impact the DCFC performance. This study concludes that woody biomass is a more suitable fuel source for DCFC. Further study on optimization of DCFC operation by employing rubber wood biochar could be conducted to enhance the performance of DCFC.

5. Acknowledgment

The author would like to thank the financial support by Taylor's University research grant scheme (TRGS/ERFS/2/2016/SOE/003) and Universiti Kebangsaan Malaysia's research grant (GUP-2018-013).

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