Application of Black Liquor Derived Carbonaceous Compound as Fuel in Direct Carbon Fuel Cell

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Abstract: Direct carbon fuel cell (DCFC) with higher power efficiency and lesser emissions is being viewed as a potential clean energy source. The application of renewable biochar as fuel for DCFC is found to be feasible to replace coal or carbon black for power generation. Black liquor from the paper production might be a suitable fuel source for DCFC due to its high lignin or carbon content. In this study, the feasibility of using compound extracted from black liquor as fuel source for DCFC was investigated in the aspect of physico-chemical and electrochemical properties. Suitable pyrolysis temperature in producing biochar from black liquor compound was first investigated. Results have shown that fixed carbon and ash content increased slightly with increasing pyrolysis temperature. The ash content is made up of majority of silica as depicted in FESEM-EDX results. Oxygen containing functional group was decomposed under high pyrolysis temperature of 700°C and 800°C. Besides, biochar obtained at 500°C of pyrolysis temperature has given the highest power density of 1.22 mW cm^{-2} whereas 1.44 mW cm^{-2} was obtained from coal which was used as the control. Future work on ash removal from the black liquor prior to pyrolysis might improve the potential of black liquor derived compound as a fuel source for DCFC.

Keywords: Black liquor, biochar, pyrolysis temperature, direct carbon fuel cell

1. Introduction

Clean and renewable energy generation technology is a long sought-after alternative to replace the current fossil fuel source. Direct carbon fuel cell (DCFC) which uses carbon as a fuel to generate electricity, is regarded as a more environmental benign process compared to the traditional carbon burning methods such as coal firing despite the release of carbon dioxide during the process. DCFC is being viewed as a clean energy source that can directly convert the chemical energy of solid carbon into electrical energy [1]. The carbon capture process from DCFC is easier and at lower cost than that for the conventional power stations owing to the ease of carbon dioxide collection with little or no impurity gases [2]. With higher than 80% of energy efficient, DCFC also offers other advantages such as non-corrosion prone with simpler operation comparing to its molten hydroxide and molten carbonate counterparts [3].

Among the carbon fuel source applied, commercial carbon black and charcoal have been shown proven to provide very high energy efficiency in DCFC [1, 4]. To achieve environmental sustainability, the usage of these non-renewable source has been shifted to waste or biomass, which is a more cost effective and renewable option. Past studies have indicated that biochar obtained from pyrolysis of biomass such as almond shell [5], rice husk [6] and olive wood [7] are the potential fuel source achieving high power density in DCFC. The type and structure of carbon fuel affects the performance of DCFC significantly [8]. As an example, woody biochar generally produced higher maximum power density compared to non-woody biochar [9]. A high fixed carbon content in the biochar is desired for higher fuel value

[10]. Lignocellulosic composition analysis indicated that the high lignin and carbohydrate contents in the biomass source, such as woody biochar, has contributed to the fixed carbon after pyrolysis process [8].

In view of this, we identify the potential of lignin retrieved from the chemical solution of pretreatment of biomass as the raw material for DCFC fuel production. One of these sources that can be utilized is the black liquor, which is the wastewater discharged from alkaline Kraft process in paper making. The composition of black liquor generally consists of high content of lignin residues (25 – 35 wt.%), hemicellulose and inorganic chemicals such as sodium hydroxide, sodium carbonate, sodium sulphide and sodium sulphate [11]. In commercial paper and pulp industry, black liquor is utilized in recovery boiler to generate electricity and steam for the plant while recovering the solvent for pulp treatment. The limitations however with the current practice include low energy conversion, corrosion of equipment and sulphur gases emissions [12].

The resources in black liquor can be recovered and converted to other value-added products such as solid acid catalyst and activated carbon as reported [13 - 14]. Till date, there is no report on retrieving the carbonaceous compound from black liquor to be implemented as fuel source in DCFC. In this study, the feasibility of utilizing carbonaceous compound derived from black liquor as fuel source for DCFC will be examined. Suitable pyrolysis condition in producing biochar from black liquor compound will first be investigated. The characteristics of biochar derived will be examined by proximate analysis, Fourier Transform infrared spectrometry (FTIR) analysis, morphology, and elemental composition analysis. The characteristic of the carbon fuel is further related to the DCFC performance, analyzed in terms of maximum power density and open circuit potential.

2. Materials and methods

2.1 Materials

Black liquor from sodium hydroxide (NaOH) pre-treatment of rice straw for paper making purpose was collected. The NaOH pretreatment was conducted at 90°C for 40 minutes with NaOH concentration in the range of 5-25%. Sulphuric acid (H_2SO_4) with 98% purity used in acidification of black liquor was from Friedemann Schmidt Chemical, Malaysia. Standard charcoal used as control was from Sigma-Aldrich. Button cell and silver wire were procured from Ningbo SOFCMAN Energy Technology Co. Ltd and KGC Resources Sdn. Bhd. respectively for DCFC analysis.

2.2 Lignin Extraction from black liquor

Concentrated H_2SO_4 was added drop by drop into 500 mL black liquor under constant agitation until pH 2 was achieved. Subsequently, the precipitated black liquor was left for sedimentation. The solution was then centrifuged at 8000 rpm for 15 min. The solid compound collected at the bottom of centrifuge tube was then washed with distilled water until pH 5 was obtained. The solid compound was then dried in oven at 85°C for 24 hours and kept in desiccator for further use.

2.3 Biochar Preparation

4g of dried solid compound extracted from black liquor was loaded into the alumina crucible. Slow pyrolysis process was conducted by using a horizontal split tube furnace (HST 1200, Carbolite) under nitrogen feed flow of 1 L min^{-1}. Pyrolysis temperature at 400, 500, 600, 700 and 800°C with a constant heating rate of 5°C min^{-1} for 1 hour were applied. The synthesized biochar was collected and stored in a desiccator to avoid moisture absorption. The cooled biochar was then weighted together with the alumina crucible to determine the biochar yield as shown in Equation 1.

$$Biochar\ yield\ (\%) = \frac{mass\ of\ biochar}{mass\ of\ compound\ extracted\ from\ black\ liquor} \times 100 \qquad (1)$$

2.4 DCFC Setup

The DCFC setup for electrochemical test of this study as shown in Fig. 1. The cathode is made up of lanthanum strontium manganite with thickness of 25 μm where anode is made up of nickel-yttria stabilized zirconia with 400 μm thickness. Yttria-stabilized zirconia with a thickness of 15 μm is used as the electrolyte. A button cell was placed in the cell holder and was activated in the absence of sample. 300 mg of biochar was loaded on the anode of the button cell. Silver wires were used as current collector connected at both anode and cathode of fuel cell. Mechanical compression was used to connect for the anode and cathode alumina tube. Nitrogen gas was fed at anode at 200 mL min^{-1} while purified air was fed at cathode at 200 mL min^{-1}. The fuel cell system was heated to 850°C at a heating rate of 10°C min^{-1}. The electrochemical performance was analyzed through potentiostat (Gamry, Interface 1000E). Once the target temperature was reached, the open circuit potential (OCP) was measured and was followed by I-V performance evaluation through a scan rate of 1mV s^{-1} on the potentiostat. Standard charcoal was used as control in this study.
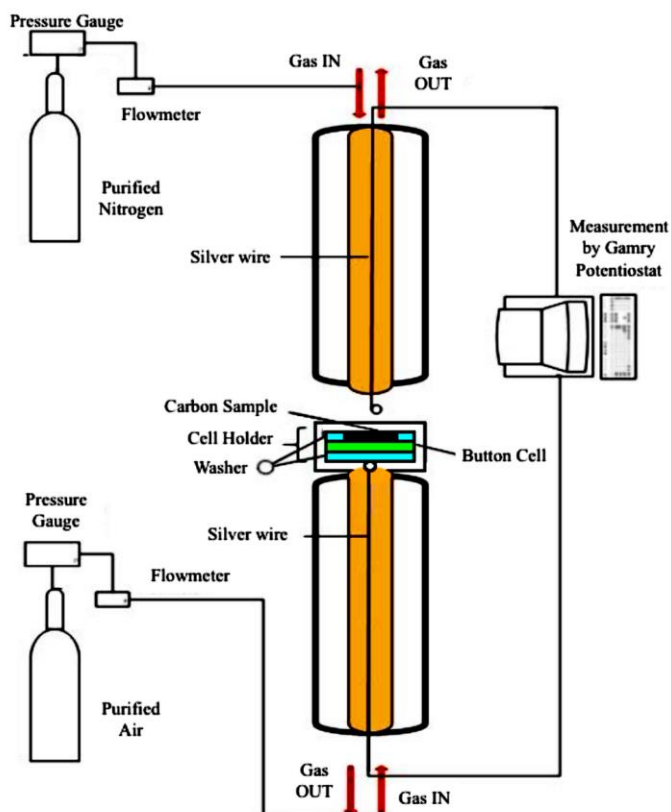
Fig. 1 - DCFC setup [15].

2.5 Characterization of Biochar

2.5.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was used for proximate analysis of biochar samples. 5 mg of sample was loaded in a ceramic crucible and placed on thermogravimetric analyzer (STA 6000, Perkin Elmer). Nitrogen gas was introduced at 0.05 L min^{-1} into the analyzer. The sample was initially heated up from room temperature to 110°C at a heating rate of 10°C min^{-1}. The temperature was then hold at 110°C for 20 minutes for moisture removal. The procedure was continued with heating until 950°C is reached under 10°C min^{-1} of heating rate. After 950°C, nitrogen gas flow was switched to purified air with a holding time of 70 min to ensure that the sample was completely decomposed. Weight loss was observed for the biochar and non-pyrolyzed compound extracted from black liquor.

2.5.2 Fourier Transform Infrared (FTIR) Spectroscopy

The changes in surface functional groups of synthesized biochar were analyzed by using Fourier transform infrared (FTIR) spectroscopy (Spectrum 100, Perkin Elmer). Attenuated total reflectance (ATR) method was used to obtain the spectra in a frequency range of 4000 cm^{-1} to 525 cm^{-1} for 16 scans at a resolution of 4 cm^{-1}.

2.5.3 Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-ray (EDX) Analysis

Field Emission Scanning Electron Microscope (HITACHI from Japan, SU8010) with two detectors and EDX (HORIBA, X-max) at a voltage of 10 kV were used to analyze the morphology and elemental composition of non-pyrolyzed compound and biochar. The platinum coated samples were applied for morphology analysis with 20k and 50k magnification. The process was then continued with elemental composition analysis through EDX with images of 20k magnification.

3. Results and Discussion

3.1 Biochar Production from Compound Extracted from Black Liquor

The compound extracted from black liquor through acidification is subjected to slow pyrolysis for biochar production. Biochar yield obtained under different pyrolysis temperature is shown in Table 1. As pyrolysis temperature increases, biochar yield decreases gradually. This is in line with most of the studies due to volatilization of compounds

and thermal degradation of lignin content with an increased temperature [16]. The biochar yield reduced from 65.4% to 54.0% when pyrolysis temperature varies from 400°C to 800°C. As compare with the results of biochar yields from biomass, the biochar yields in this study are relatively higher (>50%) while the biochar yield derived from biomass such as rice husk, palm fiber, and wheat straw are normally lesser than 40% [15, 17, 18]. The higher lignin content in the compounds derived from black liquor might be contributing to the higher biochar yield in this study.

Table 1 - Biochar yield obtained under different pyrolysis temperature

Pyrolysis temperature (°C)	400	500	600	700	800
Biochar yield (%)	65.4	59.4	56.7	55.4	54.0

3.2 Proximate Analysis on Biochar Derived from Black Liquor

The proximate analysis of non-pyrolyzed compound derived from black liquor and biochar synthesized under different pyrolysis temperature are depicted from the results obtained from thermogravimetric analysis. As shown in Table 2, the non-pyrolyzed compound has a volatile matter and fixed carbon contents of 54.48% and 16.17% respectively. After pyrolysis, the amount of volatile matter reduced drastically alongside with an increase in fixed carbon content.

As pyrolysis temperature increases from 400 to 800°C, volatile matter reduces from 22.07% to 8.74%. On the contrary, fixed carbon increases slightly when pyrolysis temperature increases. On a downside, ash content increases in biochar compared to its non-pyrolyzed counterpart. Generally, a good fuel source is known to possess high fixed carbon content with low amount of ash [4, 8]. Excessive ash content in biochar sample will hamper the DCFC operation when deposited on the anode of the cell [19]. Hence, biochar pyrolyzed at 500°C is further analyzed by using FESEM-EDX analysis to ascertain the composition of the ash and to study its impact on the performance of DCFC operation.

Table 2 - Proximate analysis of non-pyrolyzed compound and biochar derived from black liquor

Samples	Moisture (%)	Volatile Matter (%)	Fixed Carbon (%)	Ash (%)
Non-pyrolyzed compound	4.31	54.48	16.17	24.27
400°C Biochar	3.23	22.07	36.03	38.22
500°C Biochar	5.42	16.14	39.16	38.64
600°C Biochar	5.83	13.28	39.01	41.40
700°C Biochar	5.24	9.12	42.11	42.90
800°C Biochar	5.43	8.74	41.75	43.67

3.3 Surface Functional Groups Analysis

FTIR analysis was used to investigate the surface functional group of black liquor derived carbon compound. Fig. 2 illustrates the FTIR spectra of non-pyrolyzed compound and biochar from different pyrolysis temperatures. All the samples have similar spectra except for biochar produced under 700°C and 800°C. The peak between 3200 cm^{-1} to 3700 cm^{-1} attributes to the hydroxyl (O-H) stretching, which might indicate the presence of moisture in biochar [20]. The intensity of this peak does not differ much, in good agreement with the reported moisture content via proximate analysis in Table 2. The peak exists between 2700 cm^{-1} to 3000 cm^{-1} indicates the presence of aliphatic C-H stretching in all biochar samples [9]. Besides that, a new peak was formed at the range of 2400 cm^{-1} to 2000 cm^{-1} when the black liquor-extracted compound undergoes pyrolysis. The formation of peak characterizes to O=C=O, C - C and C - N stretching [21], possibly attributed to the effect of volatile removal at high temperature pyrolysis and leads to the new bonds' formation with carbon.

As the pyrolysis temperature increased, the intensity of some peaks decrease with broadening occurs. This might indicate that some of the functional groups on biochar has started to decompose. Another sharp peak was found at 1586 cm^{-1} on the biochar produced at 800°C, which was absent in all other samples. This absorption band is mostly characterized as the stretching of aromatic C=C bonding and carbonyl group (C=O) which refers to the combination of both phenyl and carbonyl compound in lignin, as well as dehydration and cyclisation when pyrolysis take place [20, 22].

Another functional group at 1200 cm^{-1} corresponds to the CO bonding for alcohol and ether group. This oxygen-containing functional group started to decompose under high pyrolysis temperature [23]. In further analysis, this might be the occurrence of thermal decomposition where the functional group had been converted into the volatile matter and

was removed under high temperature. Studies has shown that the presence of oxygen functional group in carbon fuel could increase its reactivity in electrochemical reaction as well as provide a better performance in DCFC [24, 25]. Therefore, the performance of biochar pyrolyzed at higher temperature might be negatively impacting DCFC performance due to the reduction in the surface oxygen functional group. In addition, as the temperature goes higher, broad peaks with increasing intensity was formed at 1056-1090 cm^{-1} (Si-O-Si) and 780 cm^{-1} (Si-H), indicating the presence of silica in the biochar [9]. The high ash content reported in proximate analysis might be contributed by high silica content in the raw material as the black liquor is originated from rice straw.
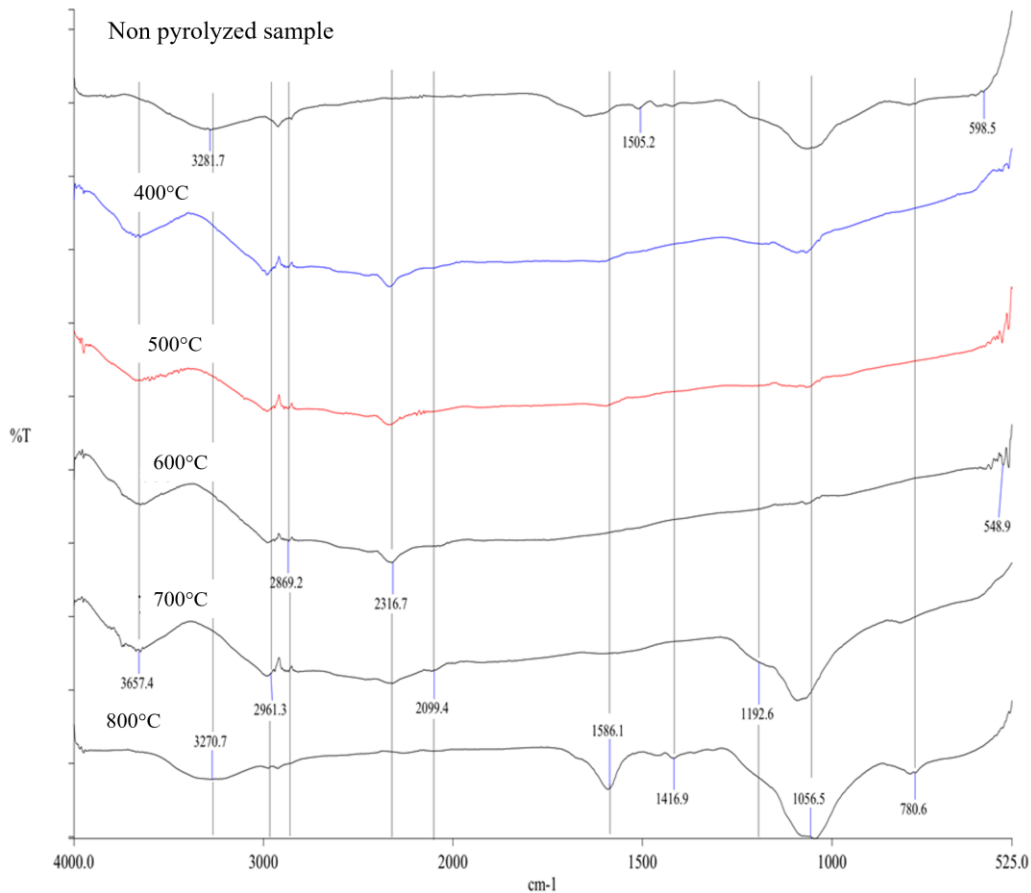

Fig. 2 - FTIR spectra for untreated carbonaceous compound and biochar from different pyrolysis temperature

3.4 DCFC Performances Test and Analysis

The non-pyrolyzed compound extracted from black liquor and biochar samples were subjected to DCFC performance analysis at operating temperature of 850°C. Fig. 3 and 4 shows the polarization curve for all the samples, with coal used as control. The open circuit potentials (OCP) of all samples are reported to be 0.80 V, except for biochar pyrolyzed at 400°C (0.77 V) and 800°C (0.74 V). The V-I curves obtained on all the samples except coal, demonstrated fluctuation in power generation, likely attributed to the poorer interfacial contact between the biochar particles and the electrode surface. In this work, the biochar particles are found coarser as compared to coal powder. Smaller particle size would generally improve the stability of DCFC performance [26]. Meanwhile, the pyrolysis temperature for preparation of biochar derived from black liquor compound has demonstrated a significant effect towards the power generation.

Black liquor compound pyrolyzed at 500°C has demonstrated the highest maximum power density of 1.22 mW/cm^2 among all samples, followed by that pyrolyzed at 600°C (1.06 mW/cm^2). However, the latter sample demonstrated quick voltage drop to zero after reaching the maximum current density of 2.7 mA/cm^2, attributed to the mass transport limitation [27]. At pyrolysis temperature of 700°C and above, it observed a rapid voltage drop with small increase in current loading. Based on proximate analysis, pyrolysis at 700 and 800°C has led to huge reduction in volatile matter despite increasing fixed carbon content slightly, along with further increase in the ash content. Previous work has demonstrated similar trends on the deteriorating effect towards DCFC power density, with reduction in volatile matter and increment in ash content, observed in rice husk-derived biochar samples [9]. In addition, the diminishing oxygen containing functional groups at high pyrolysis temperature as observed in FTIR analysis could attribute to the decrease

in the power density as well. Meanwhile, the non-pyrolyzed sample and that pyrolyzed at 400 °C, demonstrated the power density of 0.7- 0.8 mW/cm^2 with more stable V-I curve obtained. The lower ash content in the non-pyrolyzed sample indicates less obstruction on the mass transport with the presence of non-conductive and reactive silica. Pretreatment that removes ashes and increases the fixed carbon content might improve the performance of DCFC if biochar derived from black liquor is to be considered.
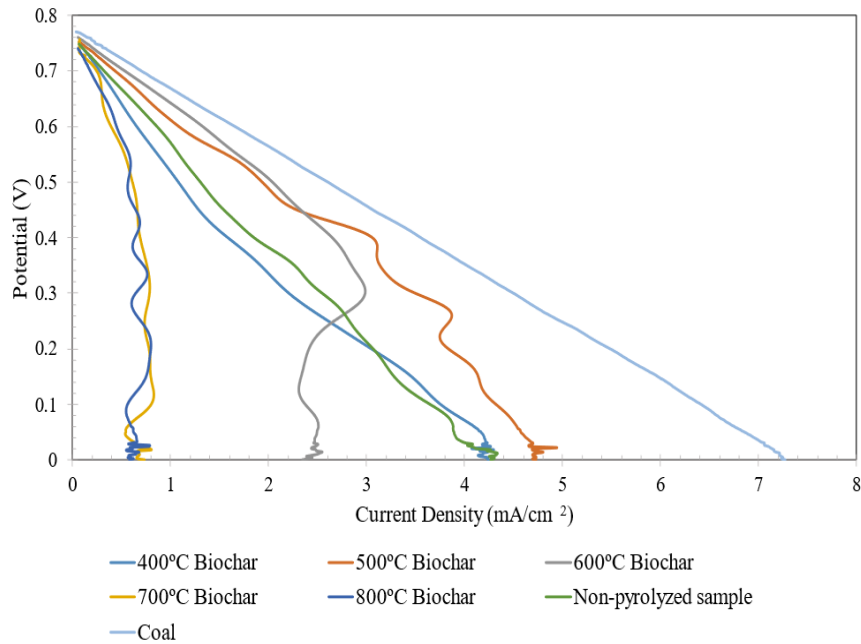

Fig. 3 - Polarization curve of black liquor derived biochar and non-pyrolyzed sample with coal used as control
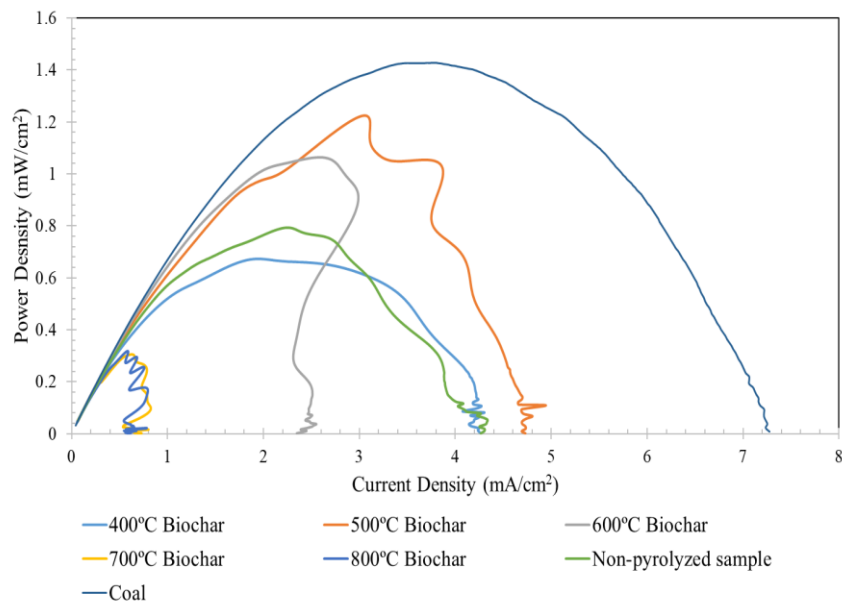

Fig. 4 - Power density curve of black liquor derived biochar and non-pyrolyzed sample with coal used as control

Table 3 shows the summary of the electrochemical performance for the coal, non-pyrolyzed sample and biochar that derived from black liquor in DCFC at 850°C. From this study, 500°C is the most suitable pyrolysis temperature as its biochar produced the largest maximum power density and current density among the biochar samples. The best pyrolysis temperature for biochar production from coconut and rice husk biomass is reported to be in the range of 500°C to 600°C [15, 28]. This shows that biochar undergoes pyrolyzed at 500°C to 600°C is the most suitable for DCFC application.

3.5 Surface Morphology Analysis on Pyrolyzed Black Liquor Derived Compound

The morphology and elemental composition analysis of the best performance biochar (500°C biochar) and non-pyrolyzed sample was studied through FESEM and EDX analysis. Fig. 5 displays the surface morphology images captured under FESEM. In Fig. 5(c), a rough and uneven surface could be observed on the non-pyrolyzed carbonaceous compound. A more porous structure was observed for biochar generated at 500°C. The formation of porous structure probably contributed by the release of volatile matters during pyrolysis process [29]. As reported in literature, the presence of high porosity would increase the electrochemical reactivity in fuel cell by providing more active sites for the reaction [30]. Hence, it is possible that the higher power density obtained from 500°C biochar than non-pyrolyzed sample is also attributed to this factor.

Table 3 - Electrochemical data from DCFC at 850°C for various samples

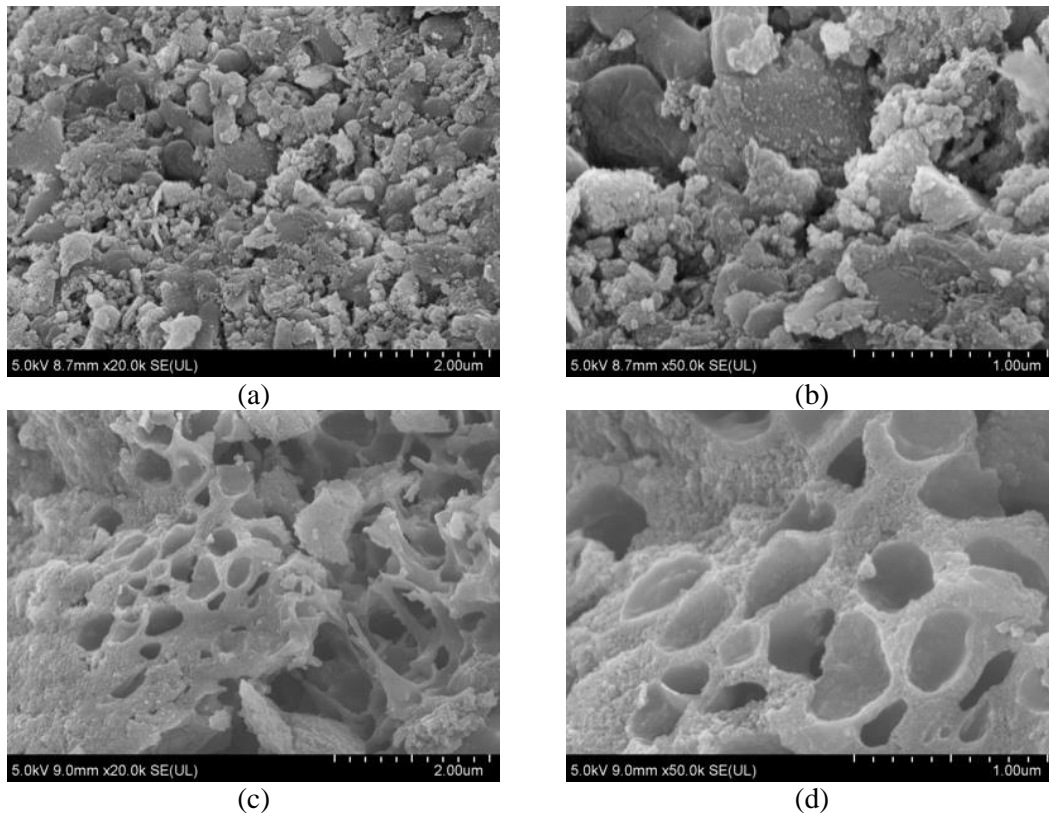| Carbon Fuel	OCP (mV)	I at 0.7mV (mA cm^{-2})	I at 0.4mV (mA cm^{-2})	I at 0.1mV (mA cm^{-2})	Power Density (mW cm^{-2})
Non-pyrolyzed sample	0.80	0.32	1.85	3.65	0.79
400°C Biochar	0.77	0.28	1.59	3.76	0.67
500°C Biochar	0.80	0.43	3.06	4.32	1.22
600°C Biochar	0.80	0.53	2.66	2.38	1.06
700°C Biochar	0.80	0.24	0.69	0.80	0.31
800°C Biochar	0.74	0.18	0.63	0.56	0.32
Coal	0.80	0.71	3.56	6.42	1.43

(a)

(b)

(c)

(d)

Fig. 5 - FESEM images: Non-pyrolyzed compound: (a) 20k magnification; (b) 50k magnification; biochar produced at 500°C: (c) 20k magnification, (d) 50k magnification

The elemental composition of non-pyrolyzed sample and 500°C biochar which under FESEM with 20k magnification are recorded in Table 4 and Fig. 6. The presence of platinum element (Pt) in all the samples was due to the platinum coating on the samples. Besides carbon and oxygen which present normally in Kraft lignin samples, other elements including magnesium (Mg), Silica (Si), potassium (K), and calcium (Ca) are found in the samples. These might be originated from rice straw raw material and the process of alkaline pretreatment. The changes in morphology, the surface elemental composition of the carbonaceous compound might also change due to the alteration of the surface

functional group in high pyrolysis temperature which had been discussed in section 3.3. In pyrolyzed sample, both carbon and oxygen contents increased slightly. The higher oxygen content in the biochar shows that could be attributed to the higher amount of oxygen functional group on its surface which could improve DCFC performance. Besides that, EDX analysis also show that the high ash content shown in thermogravimetric analysis could be proven that majorly build up by silica. Minerals such as Ca and Mg which present in both samples could be beneficial as active catalysts for electrochemical reaction [31].

Table 3 - EDX analysis of non-pyrolyzed compound and biochar produced at 500°C

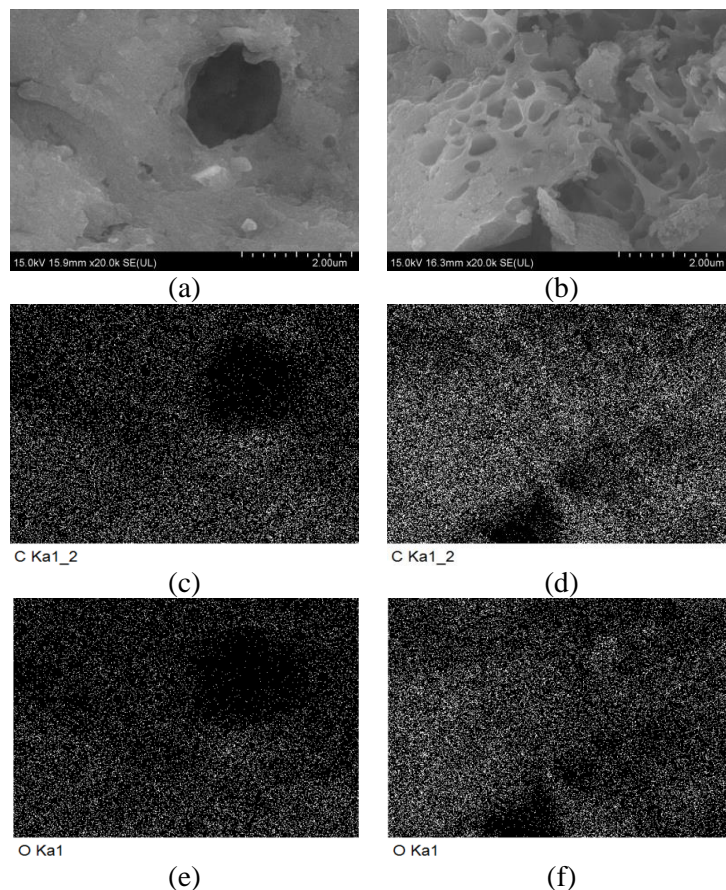| Element	Weight percent, %	
	Non-pyrolyzed compound	Biochar produced at 500°C
C	54.36	56.82
O	29.65	30.02
Mg	0.03	0.05
Si	13.15	11.94
S	0.44	0.07
K	0.05	0.02
Ca	0.04	0.01
Pt	2.29	1.01
Na	-	-

Fig. 6 - FESEM images of (a) unpyrolysed compound, (b) 500°C biochar with EDX analysis at 20k magnification where (c) and (d) represents carbon distribution while (e) and (f) represents oxygen distribution respectively

3.6 Comparison with other Biochar as Fuel Source

Some comparisons were made based on physicochemical and electrochemical characteristic of carbon fuel from others literature as listed in Table 5. Black liquor-derived biochar pyrolyzed under 500°C in current study has the lower power density compared to most of the carbon fuel used in other studies. This could be attributed to the high ash

content among the carbon fuel used in other reports that has critically hamper its chemical reactivity. Similar results could be observed in a study by Palniandy et al. [9] when rice husk biochar is producing a much lower power density compared to rubber wood biochar which might be attributed by the high ash content. It is interesting to observe that, the black liquor-derived biochar shows better power density than rice husk-derived biochar despite higher ash content present on the sample. This could be attributed to the ease of highly porous biochar formed from the liquor form of lignin, leading to increase in reactive site density on the biochar.

Another factor that causes the difference in electrochemical performance results is the different setup of DCFC used. As an example, the electrolyte used by other studies in Table 5 include molten alkaline and molten carbonate to improve the contact of solid fuel with anode [5, 32]. Different setup and electrolyte used will have significant impact on the performance of DCFC. On the other hand, the OCP obtained from black liquor biochar is comparable with other fuel sources. This shows that the black liquor-derived biochar is still a feasible candidate for DCFC operation.

Table 5 - Electrochemical data from DCFC at 850°C for various samples

Carbon Fuel	Fixed carbon (%)	Ash content (%)	OCP (V)	Power density (mW cm^{-2})	Reference
Palm mesocarp biochar, with pretreatment at 2 M HCl	73.1	6.1	0.89	5.7	[25]
Rubber wood biochar	62.0	2.0	0.76	2.21	[9]
Rice husk biochar	41.6	35.1	0.86	0.08	[9]
Bamboo-based carbon	69.12	14.53	-	13.8	[4]
Almond shell biochar	71.8	6.4	1.07	127	[5]
Apple biochar	80.3*	10.7	1.00	22.40	[32]
Sunflower husk biochar	84.1*	9.0	1.05	18.30	[32]
Pine biochar	90.4*	2.5	0.87	19.70	[32]
Black liquor derived biochar	39.2	38.6	0.80	1.22	This study

* Carbon content was obtained from ultimate analysis.

4. Conclusion

In summary, black liquor has been studied as the potential biochar fuel for DCFC application. This study revealed that the pyrolysis temperature plays a main factor in determining the biochar properties used as carbon fuel. The high porosity formed on the black liquor pyrolyzed at 500 °C, with a good composition of volatile and fixed carbon content, give rise to the reaction active sites on the biochar. From this work, it is found that the black liquor sample shows better power density than rice husk-derived biochar despite higher ash content present on the sample. To further unleash the potential of black liquor as biochar source, further works on ash removal from the black liquor prior to pyrolysis is required, which may lead to higher DCFC performance.

Acknowledgement

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