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P2B-04: ELECTROCHEMICAL PERFORMANCE OF MELON SEED HUSK WASTE BIOCHAR IN A DIRECT CARBON FUEL CELL

Ijagbulu O.M., *Adeniyi, O.D., Uthman H., Adeniyi, M.I., and Yakubu E., Chemical Engineering Department, Federal University of Technology, Minna, Nigeria *Corresponding author: o.adeniyi@futminna.edu.ng

ABSTRACT

This paper reports the study on the use of the direct carbon fuel cell (DCFC) technology to convert the chemical energy of melon seed husk (MSH) waste to electrical energy with the aim of alleviating the problem of power instability in the country. Pyrolysis was carried out on the MSH at 500°C and a heating rate of 10°C/min to produce carbon biochar used in the DCFC to produce electricity. The pyrolysed biomass was used to determine the electrochemical performances of the DCFC using molten carbonate salts as the electrolyte and five different resistor loads. The electrochemical performances of the MSH waste were investigated at a temperature of 500°C to 800°C. The biochar from the MSH waste gave an open circuit voltage of 0.68 V, a current density of 32.65 mA/cm² and power density of 7.51 mW/cm². Scanning electron microscopy (SEM) results of the carbon fuel show the morphological structures of the biofuel used in the DCFC. The phase composition using X-ray diffraction (XRD) of the biochar show some level of amorphous structure.

Keywords: Direct Carbon Fuel Cell, Melon seed husk, biochar, pyrolysis, power density

1.0 INTRODUCTION

The requirement for electrical energy for industrial and commercial need has been on the increase and according to the World Energy Council (WEC), the global demand for energy supplies will increase by over 65% in 2050 going by the current trend (WEC, 2015). Energy production from fossil fuel is on the decline as the world reserves of crude oil is declining with increase in greenhouse gas emissions. This has led to different researches in finding alternatives for electricity generation process. One of the promising alternative available is the use of fuel cell technologies particularly the direct carbon fuel cell (DCFC). A fuel cell is an electrochemical device that can convert chemical energy to electrical energy. There are different types of fuel cells but this paper focuses on the direct carbon fuel cell (Dudek *et.al.*, 2018; Adeniyi *et.al.*, 2014; Adeniyi and Ewan, 2012; Jain *et.al.*, 2009,2007).

A direct carbon fuel cell is an electrochemical device that efficiently converts the chemical energy of a carbon rich fuel (like the one present in MSH waste) directly to electrical energy without burning the fuel. The DCFC technology offer a viable technique that can produces electricity that is safe, efficient and environmentally friendly (Kacprzak *et al.*, 2017; Munnings *et.al.*, 2014; Arenillas *et.al.*, 2013; Li *et.al.*, 2010; Cooper and Berner, 2005).

Scarcity of traditional petroleum fuels and its over-dependence by nations like Nigeria, increasing emissions of combustion generated pollutants and their increasing costs have made renewable energy sources the focal point of some researchers. The world petroleum reserves are finite in nature and reducing quickly, melon seed husk a popular waste in Nigeria is a good alternate to investigate. It is an agricultural waste which is combusted in open air or dumped in refuse dumps and landfill sites thereby worsening the prevalence of greenhouse gases and becomes an

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environmental burden of pollutant emissions. There is a growing need to explore more routes for the conversion of agricultural waste such as melon seed husk for present and future clean bioenergy application (Giddey *et al.*, 2012; Jia *et.al.*, 2010; Declaux *et.al.*, 2010; Cooper and Cherepy, 2008; Cao *et al.*, 2007; Dicks, 2006; Cherepy *et al.*, 2005; Zecevic *et al.*, 2004; Larminie and Dicks, 2003; Hoogers, 2003). This paper is aimed at producing electrical energy from waste generated from MSH thereby solving the problems of environmental pollution and climate change.

2.0 METHODOLOGY

Pretreatment such as sorting, drying and size reduction were carried out for the purpose of conversion of the melon seed husk (MSH) to produce biochar from the waste using pyrolysis process. The melon seed husk waste was obtained from Kasuan Gwari, Minna, Niger State. The sample was sorted to remove impurities, dried for 48 hours, the melon seed husk was (Plates I and II) then reduced to smaller sizes of 10-15 mm. The ground samples were further sieved. The sieving process was carried out by putting the sample in the sieve with mechanical shaker to achieve uniform particle size of 8-10 mm. This process was repeated to obtain reasonable size. The ground melon seed husk was pyrolysed at 600 °C at Badeggi Research Institute, Bida, Niger State. The biochar produced after pyrolysis was ground to finer particles. Proximate analysis was carried out using an ELTRA CHS-580 Analyser (Netherlands). Samples of the biochar produced were used to determine the carbon, hydrogen, sulphur, nitrogen and oxygen contents. The proximate analyses gave the ash content, volatile matter, fixed carbon content, and moisture content using ELTRA CHS-580 Analyzer (Netherlands).

Scanning electron microscopy (SEM) (Nova NanoSEM 200 FEI, Netherlands) was used to examine the morphological structure (amorphous or crystalline structures) of the pyrolysed melon seed husk and its elemental compositions for its application as fuel in a DCFC. X-ray diffraction (Siemens D500 XRD, Netherlands) analysis was equally carried out to determine structural changes related to pyrolysed melon seed husk. XRD analysis gave the structure of the biochar produced.

The carbon biochar particles (Plate III) used for the electrochemical reaction according to procedures described in literatures (Adeniyi and Ewan, 2012; Cooper and Cherepy, 2008) was mixed with carbonate salt (15 wt.% of biomass, 46.6 wt.% of Na₂CO₃ and 53.4 wt.% of K₂CO₃. Sodium carbonate (13.98 g) and potassium carbonate (16.02 g) were mixed together and later mixed with 4.5 g of the carbon particle to form fuel for the DCFC. The electrolyte was prepared using molten carbonate of sodium and potassium based on information from literatures (Adeniyi et al., 2014; Cooper and Berner, 2005). 9.5 g of Na₂CO₃ and 15.5 g of K₂CO₃ were measured and mixed together and later transferred to a stainless steel. The mixture was stirred continuously to ensured homogeneity. The molten state of the salts was observed at a temperature range of 1159°C to 1310°C. The 25 mm aluminum wire mesh was saturated with the molten carbonate. Upon cooling, the molten carbonate stuck to the aluminum wire mesh and it was used as the electrolyte. Plates I to III show the raw MSH waste, the ground MSH and the pyrolysed MSH to produce the biochar used in the electrochemical performance in the DCFC.







Plate I: Melon seed husk

Plate II: Ground Melon Seed Husk

Plate III: Pyrolysed Melon Seed Husk

3.0 RESULTS AND DISCUSSIONS

Table 1 shows the proximate analysis results on the pyrolysed MSH showing the chemical composition. This includes the percentage of the volatile content (VC), ash content (AC), moisture content (MC), and fixed carbon (FC). Ultimate analysis was performed to determine the elemental composition of the MSH biofuel giving the Carbon (C), Nitrogen (N_2), Hydrogen (N_2), Oxygen (N_2) and Sulphur (S). The proximate and ultimate analyses were carried out at the National Cereal Research Institute (NCRI), Badeggi, Niger State. The higher heating value (HHV) is also presented. The carbon and the higher heating values are significant for the performance of this biomass in the DCFC.

Table 1: Proximate and ultimate analyses for Melon Seed Husk (MSH) waste

MC	AC	VC	FC	HHV	C	H	S	N	O
wt.%	wt.%	wt.%	wt.%	MJ/kg	wt.%	wt.%	wt.%	wt.%	wt.%
2.5	5.0	66.0	26.5	18.7	41.2	3.6	39.6	1.2	0.3

Figure 1 shows the SEM micrograph for the carbon fuel particle of the biomass. The SEM results show differences in the particle sizes and porosity of the biochar. Results of the XRD from the analyses conducted on the pyrolysed MSH waste biochar are shown in Figure 2, these revealed a disordered carbon fuel structures, this is what will enhance oxidation of the carbon fuel and in turn enhance the electrochemical conversion in the DCFC. These results obtained can be used to explain variation in the size distribution and structure of the MSH biochar. Figure 2 shows the XRD of pyrolysed melon seed husks used in fuel cell. The highest peak occurred at angle of 33.1 (2θ axis) and relative intensity of 100 %. The XRD pattern reveals that the MSH biochar is amorphous in nature, which will enhance the electrochemical conversion of the fuel during fuel cell operations. There are also indications of crystalline structures in the figure suggesting the presence of impurities like silica.

Table 1 show the MSH waste proximate and ultimate values, of significant interest is the HHV and the carbon content which are important parameters for the fuel used in the DCFC. Tables 2 and 3 show the open circuit voltage (OCV) result from the electrochemical conversion of the MSH biochar in the DCFC. The OCV is the voltage of the fuel cell when current and power densities

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are not taken out of the system. The OCV increases with the increase in temperature indicating that the oxidation of the MSH waste biofuel is favoured by temperature (Kacprzak *et al.*, 2017; Hackett *et al.*, 2007). Table 3 shows the results obtained from the electrochemical performance of the DCFC at different temperatures.

Table 2: Open Circuit Voltage (OCV) readings for Melon Seed Husk waste

S/No	Time (min)	Temperature (°C)	OCV (V)	
1	24	100	0.02	
2	48	200	0.04	
3	66	300	0.05	
4	96	400	0.06	
5	124	500	0.18	
6	132	600	0.35	
7	140	700	0.38	
8	144	800	0.68	

The OCV increased with increase in temperature of the DCFC, this is because carbon oxidation is favoured by increase in temperature (Cao *et al.*, 2007; Zecevic *et al.*, 2004). The maximum OCV was observed at 800 °C to give 0.68 V. From Table 3, the maximum current density of 32.65 mA/cm² was obtained at 800 °C, the same was observed for the peak power generation and efficiency.

Table 3: DCFC Electrochemical performance at different temperature

Temperature (°C)							
Cell parameters	500	600	700	800			
OCV (V)	0.18	0.35	0.38	0.68			
Peak power density (mW/cm ²)	1.71	3.82	5.33	7.51			
Max. current density (mA/cm ²)	16.33	20.57	24.49	32.65			
Voltage at peak power (V)	0.08	0.17	0.19	0.46			
Efficiency at peak power (%)	22.0	49.0	50.0	68.0			



Figure 1: SEM Melon Seed Husk waste biofuel

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Figure 3 shows the OCV results obtained from the experiment carried out on the DCFC at varying temperature from 100 °C to 800 °C. As the temperature increase from 100–800 °C it was observed that there was an increase in value but a reasonable increase was noticed from 400 °C to 800 °C, this was as a result of the electrons movement and conduction of electricity, leading to the biochar reaching the electrolytes assembly to take part in the electrochemical conversion. It has been reported that carbon oxidation is favoured by temperature (Dudek *et.al.*, 2018; Adeniyi *et.al.*, 2014; Jain *et.al.*, 2009, 2007).

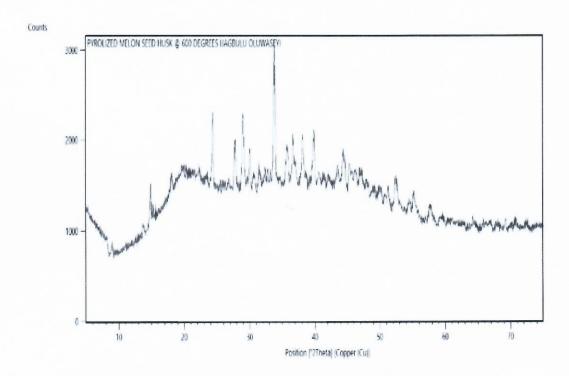


Figure 2: XRD of Melon Seed Husk waste biofuel

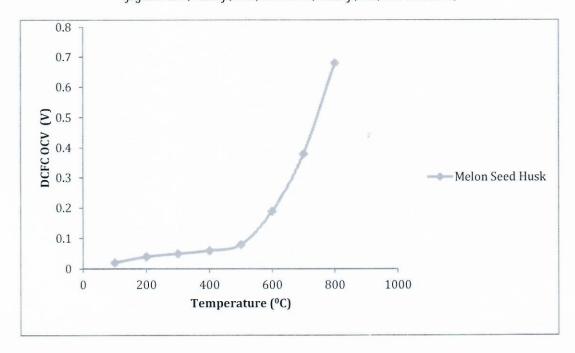


Figure 3: DCFC-OCV for the MSH waste biofuel at various temperatures.

Figure 4 presents the results obtained from the electrochemical performance of the MSH biochar in the direct carbon fuel cell. The tests were conducted at various temperatures of $500\,^{\circ}$ C, $600\,^{\circ}$ C, $700\,^{\circ}$ C and $800\,^{\circ}$ C. From Figure 4, the DCFC current density and power density increases with increase in the operating temperature. These observations were similar to those in the literature (Li *et al.*, 2010; Hackett *et al.*, 2007). At $800\,^{\circ}$ C, the electrochemical performance was much better and improved as a result of the improvement in the conduction rate of the ions of the electrolyte and the electrochemical reactions at the two electrodes of the DCFC (Li *et al.*, 2010; Hackett *et al.*, 2007).

Figures 3 and 4 present the electrochemical performances of the MSH waste biochar utilized in the molten carbonate direct carbon fuel cell. The open circuit voltage increased (0.18 V at 500 °C) with the increase in the temperature until it reached its maximum (0.68 V at 800 °C). At 800 °C the peak values obtained for the current density and power density were 32.65 mA/cm² and 7.51 mW/cm². At 800 °C, the greater part of the carbon fuel was consumed requiring a refill for further electrochemical reactions (Munnings *et al.*, 2014; Jia *et al.*, 2010; Jain *et al.*, 2009).

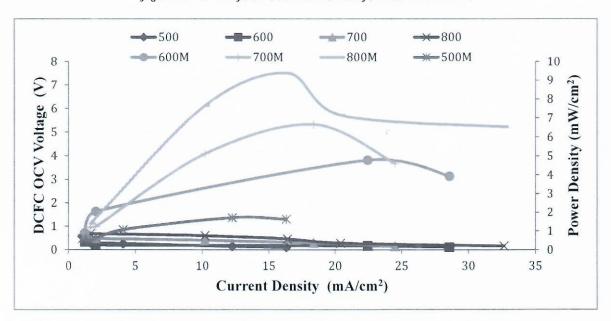


Figure 4: DCFC performances using MSH biochar at different temperatures

4.0 CONCLUSIONS

The study of the molten carbonate direct fuel cell showing the electrochemical performance of melon seed husk (MSH) waste biochar was carried out. The highest open circuit voltage of the biochar was 0.68 V showing the viability of using MSH waste biochar to power the DCFC. The optimum peak power density recorded for the biochar is 7.51 mW/cm², maximum current density of 32.65 mA/cm². An efficiency of 68 % was obtained from the MSH waste biochar which enhances the electrochemical performance in the direct carbon fuel cell operations. The scanning electron micrograph and X- ray diffraction reveals that the MSH biochar contain various sized particles with amorphous structures. It was observed that finer particle morphology led to enhanced current density and the presence of non-crystallites carbon product improved the current and power densities achievable with the direct carbon fuel cell.

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