# POWER GENERATION FROM MELON SEED HUSK BIOCHAR USING FUEL CELL

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#### ABSTRACT

Melon seed husk (MSH) biochar was used in a single cell direct carbon fuel cell (DCFC) as an alternative biofuel. The DCFCs belong to a generation of energy conversion devices that are characterised with higher efficiencies, lower emission of pollutants and MSH biochar as the fuel. Several analytical techniques (proximate, ultimate and thermo-chemical analysis) were employed to analyse the characteristics of the biomass fuel, their effects on the cell's performance, and the electrochemical reactions between the fuel and the electrolyte in the system. High carbon content and calorific values are some of the parameters responsible for good performances. The performance of a lab-scale DCFC made of ceramic tubes using molten carbonate electrolyte was investigated. Binary carbonates mixture (Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>, 38-62 mol.%) was used as electrolyte and the waste MSH carbonised at 450°C as biofuel. A practical evaluation of the fuel used in the DCFC system was conducted, for varying temperature of 100-800°C. The maximum open circuit voltage (OCV) was 0.71 V. With an applied load resistance and active surface area of 5.73 cm<sup>2</sup> the maximum power density was 5.50 mWcm<sup>-2</sup> and the current density was 29.67 mAcm<sup>-2</sup> at 800°C.

**Keywords:** Direct carbon fuel cell, Melon seed husk, voltage, biochar, current, power, electrochemical.

### Introduction

The depletion of world's energy reserves has made energy sustainability a global subject as the need for energy is ever increasing to take care of the world growing population and industrialization. The consumption of fossil fuels continues to rise, there are big concerns about the exhaustion of these resources and environmental pollution have continued to escalate globally (Giddey *et al.*, 2012; Rasul

et al., 2012). In attempts to resolve these issues, researchers have expended a lot of effort toward increasing the efficiency and developing techniques for reducing pollution via renewable energy giving preference for biomass as an alternative source of fuel (Dudek et al., 2018; Alisaraei et al., 2017; Hackett et al., 2007). Biomass has many benefits in comparison to fossil fuels. One of the key benefits of this type of fuel is the

low  $\mathrm{CO}_2$  emissions. The direct carbon fuel cell (DCFC) is a type of fuel cell that convert chemical energy into electricity through electrochemical oxidation of solid carbon at high temperature from biochar or coal (Jiao et al., 2018; Kacprzak et al., 2017; Muthuvel et al., 2009). The direct carbon fuel cell uses carbon as fuel, which is feed to the anode and it gives a higher thermal efficiency for electric power generation compared to other types of fuel cell (Cao et al., 2007). When using the molten carbonate electrolyte system in the DCFC, the electrochemical reactions are given by Equations [1-3].

$$C + 2CO_3^{2-} = 3CO_2 + 4e^-$$
 [1] (Anode)  
 $O_2 + 2CO_2 + 4e^- = 2CO_3^{2-}$  [2] (Cathode)  
 $C + O_2 = CO_2$  E°=1.02V [3] (Overall)

Solid carbon-rich fuel such as biomass, organic waste and coal are used as raw materials for powering the DCFC. And these raw materials are in abundant especially the biomass, and is also renewable (Boyle, 2004). The overall system efficiency of a DCFC, taking into account of secondary losses is within the range of 60 - 70%, compared to Carnot Cycle having efficiency of less than 40% (Giddey et al., 2012). And at higher operating temperature for a DCFCs (above 600°C), carbon fuel is electrooxidised to CO<sub>2</sub> at the anode section creating electricity (Wolk et al., 2007). This CO, comes out in its pure form without mixing with other gases and thus can be collected and used in other industrial operation such as in the food and drink industries, enhanced oil recovery and others. Molten carbonate as an electrolyte has numerous advantages over other types of electrolytes; the molten carbonate electrolyte has good long-term stability in CO2 and can catalyse carbon oxidation. It also has high ionic conductivity (Morital et al., 2010). Pyrolysis

temperature, heating rate and residence time are important in determining the biochar properties (Czernik & Bridgwater, 2004). Pyrolysis aims at inducing carbonization reaction through thermochemical process. Pyrolysis works under the absence of oxidizing agent at elevated temperature, and such requirement is achieved by purging oxidant gas using inert gas such as nitrogen for an interval before heating the reactor, creating an inert gas atmosphere (Basu, 2010).

This paper report investigations base on the research on the efficiency of a single cell DCFC operated on biofuel derived from melon seed husk (MSH). MSH waste are thrown away indiscriminately into the environment thus causing environmental pollution which could also lead to health challenges if not properly controlled. MSH is an agricultural product which is abundantly available after the melon seed is used as food and condiments. The biochar obtained from MSH has a natural porous structure which is beneficial for the DCFC electrochemical reactions.

## **Experimental**

Pre-treatment of carbon fuels

The selected biomasses of MSH wastes were collected from Nasarawa State, Northern part of Nigeria. It was then sorted to remove impurities which can affect the experiment. The MSH were dried for 48 hours before being pulverized in a rotary miller three times and then sieved with a 250 µm mesh to obtain the effective particle size before carrying out proximate and ultimate analysis.

The ash and volatile content were measured using a Carbolite furnace (AAS 1100, England) operated at temperatures of 750°C and 950°C respectively. The moisture content was determined using an oven (Mermmet, Germany) operated at 105°C for an hour and

the fixed carbon was calculated by difference. The biomass samples of particle size of 250 µm were dried at 100°C before pyrolysing in an electrically heated Carbolite furnace (AAS 1100, England). In each pyrolysis cycle, the sample was heated at a rate of 10°C/min, to the operating temperature of 800°C and held

for 30 min (Sensoz, 2003). Nitrogen gas was used to purge the system at a rate of 8 litre/min, during and after the pyrolysis process until it cooled down to 100°C. Fig. 1 shows the morphological changes that occurred to the MSH waste during pyrolysis process.







(a) Melon seed husk (MSH)

(b) Ground

(c) Biochar fuel

Fig 1: Morphological changes of melon seed biomass during pyrolysis process.

# Preparation of carbon fuel particles

The solid carbon rich fuel (char) mixed with carbonate (15 wt.% of biomass, 46.6 wt.% of Na<sub>2</sub>CO<sub>3</sub> and 53.4 wt.% of K<sub>2</sub>CO<sub>3</sub>) was used as fuel for electrochemical reaction in the DCFC as suggested by Adeniyi (2011) and Cooper (2007). About fourteen grammes (13.98 g) of sodium carbonate and 16.02 g of potassium carbonate were measured and introduced into a 25 ml distilled water to ensue homogeneous mixtures. The homogeneous mixtures were charged into an oven at 100°C for 3 hours to dry. The Na-K carbonate mixtures was ground and then mixed with 4.5 g of the biomass carbon particles to form the fuel particles for the DCFC (Adeniyi, 2011).

## Cell fabrication and operation

The anode and the cathode were made of ceramic tubes of 20 mm diameter. The use of ceramic tubes helps to retain heat and

ensure good measurement of temperature. Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> mixtures were used as the electrolyte (Cooper *et al.*, 2004) while Aluminium wire mesh of diameter 25 mm was saturated with the molten carbonate mixture at 600°C. Two copper wires embalmed with crystal beads were used to provide insulation. Each of the copper wires was placed in contact with the mesh being saturated with the molten carbonate which serves as current collectors (Adeniyi *et al.*, 2014).

The setup followed the pattern as suggested by Adeniyi (2011) in which the assembled DCFC (containing the electrolyte and the carbon fuel) was inserted into the furnace. The current collectors were attached to the resistor box and a K-type thermocouple (ESL Electro-Science, England) was used to measure the temperature of the DCFC. The DCFC was heated to a high temperature and the open circuit voltage was obtained for varying

temperatures of 100°C, 200°C, 300°C, 400°C, 500°C, 600°C, 700°C and 800°C respectively.

At a stable temperature of  $800^{\circ}$ C, the current collectors were then connected to the variable resistor box (input holes) while the output wires of the resistor were connected to the multimeter probes (Fluke 29, USA). For a varying resistor of 1.0, 1.8, 2.4, 3.9 and 4.7 k $\Omega$ , the voltage

readings were obtained and recorded. This was repeated for a stable temperature of 700°C, 600°C and 500°C respectively.

## Results and discussion

Proximate and Ultimate analysis
The results obtained for both the proximate
and ultimate analysis are shown in Table 1.

**TABLE 1**Parameter of the biochar chosen for DCFC efficiency investigation.

Analysis	Moisture content wt. %	Ash content wt. %	Volatile matter wt.		CV MJ/kg	Carbon wt. %	Hydrogen Wt. %
Biochar	3.18	2.5	39.2	57.12	22.00	51.0	7.5

## CV - Calorific Value

The low value of the ash content (2.5 wt.%) indicate that large amount of carbon present in the sample were not oxidized to CO<sub>2</sub> and this was achieved using nitrogen as a purging gas to remove any trace of oxygen in the pyrolysis reactor. Ash is an impurity that will not burn and it reduces the handling and burning capacity of the biofuel. This high volatile matter content (39.0 wt.%) indicate easy ignition of the fuel. The CV gives account of the burning rate of the fuel. The higher the CV, the higher the burning rate and the better the electrochemical reaction in the DCFC.

# Voltages of DCFC using MSH as biofuel

It was observed that as the temperature inside the DCFC increases, the open circuit voltage (OCV) also increases. At temperatures from 100 - 400°C, there was slow increment in voltage (Fig. 2).

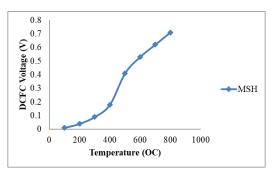


Fig. 2: DCFC open circuit voltage

## (OCV) for melon seed husk (MSH).

This could be attributed to the fact that the solid salt has not melted and as a result, the temperature is still below the level that will kindle the movement of electrons. From 500°C, there was significant rise in voltage (Fig. 2). This is because the molten salt had started melting and there were rapid movement of electrons (ionic conduction in the molten carbonate salt). This rapid increase in voltages continued up to a temperature of 800°C. This

is attributed to the fact that the salt is now in its molten form (although highly viscous) and permits the rapid electro oxidation of the carbon and movement of the electrons across the cell. The highest voltage (0.71 V) was obtained at 800°C.

## DCFC performance using MSH

The highest temperature produced the highest voltage (Fig. 3). From Fig. 3, 500V, 550V, 600V, 700V and 800V represent the voltages obtained at 500°C, 550°C, 600°C, 700°C and 800°C. The maximum voltage obtained was 0.71V at 800°C, having a current density of 30 mAcm<sup>-2</sup>. At 700°C, the highest voltage was 0.66V having a current density of 24.4 mAcm<sup>-2</sup>. At 600°C, the voltage obtained was 0.58V and its current density was 26.19 mAcm<sup>-2</sup>. This current density increased to 17.45 mAcm<sup>-2</sup> at 550°C. There were increases in voltages as current densities decreases signifying similar patterns in the DCFC operations from lower to higher temperatures.

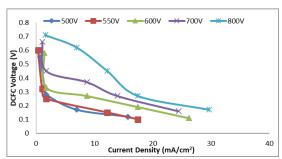


Fig. 3: Voltage and current density using MSH in DCFC at 500 °C to 800 °C.

The behaviour of the graph follows the pattern as suggested by (Adeniyi *et al.*, 2014; Adeniyi, 2011; Dicks, 2006). Different losses such as Ohmic losses concentration losses and activation losses were observed for each temperature line. There was rapid initial fall

in voltage for temperature regime of 500°C, 550°C, 600°C and 700°C as the carbonate becomes molten (Fig. 4). This rapid fall of voltage at low current could be attributed to activation losses taking place on the surface of the electrode in which a portion of the voltage being generated is used to drive electrons to and from the electrode (Adeniyi, 2011).

At 800°C, the activation loses was insignificant but Ohmic effect were still observed. After which there was a slow fall in voltage and the graph became almost linear for temperature of 500°C and 600°C with increase in current due to Ohmic losses. The slowness of reaction could be attributed to activation losses taking place on the surface of the electrode in which a portion of the voltage generated was used to drive electrons to and from the electrode (Adeniyi, 2011). The rate of voltage drop with current density affects the thermodynamic efficiency of the system; it is therefore required that the voltage remains high as current density increases. A combination of both power density, current density and the DCFC voltages are shown in Fig. 4. Also, from Fig. 4, 500P, 550P, 600P, 700P and 800P represent the power densities obtained at 500°C, 550°C, 600°C, 700°C and 800°C.

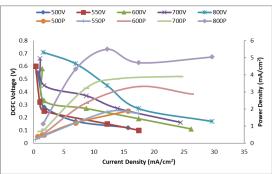


Fig. 4: Voltage, power and current densities using MSH biochar fuel at 500 °C to 800 °C.

The highest power density was 5.50 mWcm<sup>-2</sup> at a temperature regime of 800°C. The power density at 700°C reduces to 3.90 mWcm<sup>-2</sup>. This further reduces to 3.32 mWcm<sup>-2</sup> at 600°C and 1.83 mWcm<sup>-2</sup> at 550°C. At 500°C, the power density was 3.32 mWcm<sup>-2</sup>, this could be as a result of the internal changes occurring in the DCFC during the electrochemical reactions.

#### Conclusion

The direct carbon fuel cell offers some promising benefits in terms of electricity generation and environmental aspects, as compared to the conventional combustion system. The ash content obtained during pyrolysis was sufficiently low (2.5%) which implies high performance of the biochar fuel in the DCFC. The possibility of operating DCFCs by melon seed husk waste was demonstrated in terms of the open circuit voltage, current and power densities. The highest open circuit voltage obtained (0.71V) was at 800°C showing that the electrochemical conversion of MSH was enhanced with temperature. A peak power density of 5.5 mWcm<sup>-2</sup> and a maximum current density of 30 mAcm<sup>-2</sup> were obtained at 800°C. High carbon content and disordered structure of the melon seed husk biochar plays an effective role in the improvement of the cell performance.

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#### References

ADENIYI, O. D. (2011) The Use of Biomass in Molten Carbonate and Solid Oxide Direct Carbon Fuel Cell, PhD thesis, Department of Chemical and Biological Engineering, University of Sheffield, United Kingdom.

- ADENIYI, O. D., EWAN, B. C. R., ADENIYI, M. I. & ABDULKADIR, M. (2014) The behaviour of biomass char in two direct carbon fuel cell designs, *J. Ener. Challenges* & *Mechanics* 1 (4), 1 6.
- Basu, P. (2010) Biomass gasification and pyrolysis: practical design and theory. Academic Press.
- BOYLE, G. C. (2004) "Renewable energy: Power for a sustainable future", 2nd ed., Oxford University Press, Oxford, 56 60.
- Cao, D., Sun, Y. & Wang, G. (2007) "Direct Carbon Fuel Cell: Fundamentals and Recent Developments," *J. of Pow. Sources* **167** (2), 250 257.
- COOPER, J. F. (2007). Direct conversion of coal derived carbon in fuel cells. In: Basu S, editor, 17 20.
- COOPER, J. F., KRUEGER, R. & CHEREPY, N. (2004) "Fuel cell apparatus and method thereof", US Patent No. US 6815105 B2.
- Czernik, S. & Bridgwater, A. (2004) Overview of applications of biomass fast pyrolysis oil. *Energy* & Fuels **18** (2), 590 598.
- Dicks, A. L. (2006) The Role of Carbon in Fuel Cells, *J. of Pow. Sources* **156** (2), 128 141.
- Dudek, M., Adamczyk, B., Sitarz, M., Sliwa, M., Lach, R., Skrzypkiewicz, M., Razniak, A., Ziabka, M., Zuwala, J. & Grzywacz, P. (2018) The usefulness of walnut shells as waste biomass fuels in direct carbon solid oxidefuel cells, *Biom. & Bioen.* 119, 144 154.
- GIDDEY, S., BADWAL, S. P., KULKARNI, A. & MUN-NINGS, C. (2012) A comprehensive review of direct carbon fuel cell technology. *Prog. Ener.* and Comb. Sci. 38, 360 - 399.
- HACKETT, G. A., ZONDLO, J. W. & SVENSSON, R. (2007) Evaluation of carbon materials for use in a

- direct carbon fuel cell. *J Pow. Sources* **168**, 111 8.
- JIAO, Y., XUE, X., AN, W., JULIAO, P. S. B., WANG, W., YANG, G., ZHOU, W. & LI, S. D. (2018) Purified high-sulfur coal as a fuel for direct carbon fuel cell, *Int. J. Energy Res.* 1 13.
- KACPRZAK, A., KOBYLECKI, R. & BIS, Z. (2017) The effect of coal thermal pretreatment on the electrochemical performance of molten hydroxide direct carbon fuel cell (MH-DCFC), *J. Pow. Tech.* **97** (5), 382 387.
- MORITA, H., KAWASE, M., MUGIKURA, Y. & ASANO, K. (2010) Degradation mechanism of molten carbonate fuel cell based on long-term performance: Long-term operation by using bench-scale cell and post-test analysis of the cell. *J. Pow. Sources.* **195**, 6988 96.
- MUTHUVEL, M., JIN, X. & BOTTE, G. G. (2009) Fuel cells exploratory fuel cells Direct Carbon Fuel Cells. In: Jürgen G, editor. Encyclopaedia of Electrochemical Power Sources, Elsevier, 158 71.

- RASUL, M. G., JAHIRUL, M. I., CHOWDHURY, A. A. & ASHWATH, N. (2012) Biofuels Production through Biomass Pyrolysis-A Technological Review. *J. Energies* **5**, 4952 5001.
- SENSÖZ, S. (2003) "Slow pyrolysis of wood barks from Pinus brutia Ten. and product composition", *Bioresource Tech.* **89**, 307 -311.
- TAGHIZADEH-ALISARAEI, A., ASSAR, H. A., GHOBADI-AN, B. & MOTEVALI, A. (2017) Potential of biofuel production from pistachio waste in Iran, *Ren. & Sustain. Energy Reviews* **72**, 510 - 522.
- WOLK, R. H., SCOTT, L., GELBER, S. & HOLCOMB, F. H. (2007) "Direct carbon fuel cells: Converting waste to electricity". *ERDC/CERL fuel cell program*, U.S. Army Corps of Engineers, Final Report Washington D.C. Recent trends in fuel cell science and technology: Springer New York. p. 248 66.