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COMPARISON OF THE ELECTROCHEMICAL PERFORMANCES OF MCDCFC USING HAND AND BALL MILLED BIOMASS CARBON FUELS

^{*1}Olalekan D. Adeniyi, ¹Mary I. Adeniyi, ¹Moses A. Olutoye

¹Chemical Engineering Department, Federal University of Technology, PMB 65, Minna, Nigeria

^{*1} lekanadeniyi625@futminna.edu.ng

²Bruce C. R. Ewan

²Chemical and Biological Engineering Department, University of Sheffield, Sheffield, S1 3JD, U.K.

¹Joseph O. Okafor, ¹Eyitayo A. Afolabi

¹Chemical Engineering Department, Federal University of Technology, PMB 65, Minna, Nigeria

³Ayodeji A. Ayoola, ³Modupe E. Ojewumi and ³James A. Omoleye

³Chemical Engineering Department, Covenant University, Canaan land, Km 10 Idiroko Road, Ota, Nigeria

ABSTRACT

The electrochemical performances of a single cell molten carbonate electrolyte direct carbon fuel cell (MCDCFC) using miscanthus and switchgrass biomass carbon fuels subjected to hand and ball milling treatments are presented in this paper. Conventional direct carbon fuel cell (DCFC) uses carbon derived from coal, a fossil fuel with adverse consequences on the environment. This paper explores a more benign carbon fuel source which is the biomass to power the DCFC. The performances of the hand milled (HM) carbon fuels were slightly higher than those of the ball milled (BM) carbon fuels. At 800°C for the open circuit voltage, miscanthus fuel (1.03 V) has higher values for the HM and switchgrass fuel (0.77 V) for the BM. Higher peak power densities were observed for switchgrass fuel (21.60 and 12.32 mW/cm²) for both the HM and BM. Switchgrass fuel (74 mA/cm²) gave the maximum current density for both the HM and BM. Miscanthus fuel (0.72 V) show higher voltage at peak power generation for the HM and switchgrass fuel (0.39 V) for the BM. The peak power efficiency evaluated show that miscanthus fuel (70%) gave higher values for the hand milled and equal values for both carbon fuels (51%) for the ball milled.

1. INTRODUCTION

The performances of a single cell molten carbonate electrolyte direct carbon fuel cell (MCDCFC) with the biomass carbon fuels show some promising technology for the future. Coal that usually powers the DCFC is finite in nature plus the added environmental challenges of burning coal in power plant for electricity generation, these challenges can be alleviated using biomass in

MCDCFC. The molten carbonate fuel cells (MCFC) electrolyte is a mixture of alkali carbonates, mostly Li_2CO_3 and K_2CO_3 , sometimes with additions of alkaline earth carbonates, above their melting point at operating temperatures of around 650°C . The charge carrier ion in MCFC is a carbonate ion, CO_3^{2-} , moving from cathode to anode. An interesting feature of MCFC is that the depletion of carbonate ion from the cathode makes it necessary to recycle CO_2 from anode to cathode (Hoogers, 2003). The results obtained from the MCDCFC are reproducible, the variation observed in the results are due to a number of factors such as ohmic resistance, activation losses, mass transport limitation and the aging process of the electrochemical cell system as pointed out by other researchers (Adeniyi, 2015; Adeniyi *et al.*, 2014; Adeniyi and Ewan, 2012, 2011; Li *et al.*, 2011a,b; Jia *et al.*, 2010; Li *et al.*, 2009; Wu *et al.*, 2009; Hackett *et al.*, 2007; Cao *et al.*, 2007; Cherepy *et al.*, 2005; Nakagawa and Ishida, 1988).

2. METHODOLOGY

Figure 1 shows the fuel cell experimental set-up that was developed for the electrochemical operation of the molten carbonate direct carbon fuel cell (MCDCFC). The electrolyte consists of zirconia saturated in carbonated mixture (lithium carbonate and potassium carbonate). The electrode assembly is inserted in a high temperature furnace ($600\text{--}1000^\circ\text{C}$). The anode side has gold mesh collecting electrical current through the gold wire electrode. At the top is mica seal protecting the gold mesh from the anode casing. At the cathode side is a gold mesh for current collection and mica seal for protection. This electrode assembly description has been presented in previous publications (Adeniyi *et al.*, 2014; Adeniyi and Ewan, 2012, 2011).



Figure 1: MCDCFC experimental set-up.

Miscanthus and switchgrass straws were reduced to smaller pieces before grinding. Grinding was carried out using the Cross Beater Mill (Model 16-150, Glen Creston Ltd., England). The biomass samples were dried at 100°C before pyrolysing in an electrically heated cylindrical

Lenton furnace at 800°C, and the pyrolysis was monitored. The carbon/carbonate fuel mixture was prepared consisting of the char (15 wt.%), lithium and potassium carbonates. The carbonate mixture components ($\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$) were mixed in the ratio of 46.6 wt.% Li_2CO_3 and 53.4 wt.% K_2CO_3 (Adeniyi *et al.*, 2014; Adeniyi and Ewan, 2012, 2011; Wu *et al.*, 2009; Cooper and Cherepy, 2008; Cao *et al.*, 2007; Cherepy *et al.*, 2005; Ihara *et al.*, 2004).

3. RESULTS

3.1 Miscanthus (*Miscanthus x giganteus*) Carbon Fuel

The differences between the hand and ball milled biomass carbon fuels in the molten carbonate direct carbon fuel cell (MCDCFC) performances using miscanthus fuel at 600°C, 700°C and 800°C are shown in Figures 1 to 3. These figures show that the hand milled miscanthus carbon fuel exhibit better performances than the ball milled ones. Hand milled carbon fuel has average particle size of 29 μm while the ball milled were 8 μm . It was observed that at this particle sizes the effect of milling was not significant to produce better electrochemical reactions using the miscanthus fuel in the MCDCFC. The specific surface area increased from 0.57 m^2/g for the hand milled to 0.95 m^2/g for the ball milled, again this effect was not enough to enhance the electrochemical discharge rate using this carbon fuel (Cherepy *et al.*, 2005). The graphs of comparison shown here are for miscanthus (Figure 1 to 3) and switchgrass (Figure 7 to 9) biomass carbon fuels.

Figure 3 present the miscanthus fuel performance at an operating temperature of 800°C, it was observed that the hand milled fuel has high power density but low current density. The hand milled fuel was affected by the overconsumption of the carbon fuel at the anode which leads to gap between the fuel and the electrolyte surfaces and thus causing low current generation, but for this occurrence the current output could have been better (Adeniyi *et al.*, 2014; Adeniyi and Ewan, 2012, 2011; Jia *et al.*, 2010). The acronym HMP and BMV refer to the hand milled voltage and ball milled voltage. While HMP and BMP are the hand milled power density and ball milled power density. Figures 4 and 5 show the SEM micrographs of the miscanthus carbon fuels. These micrographs showed that there are different particle sizes and shapes, the connectivity of the particles in aggregates for the hand and ball milled carbon fuels look similar.

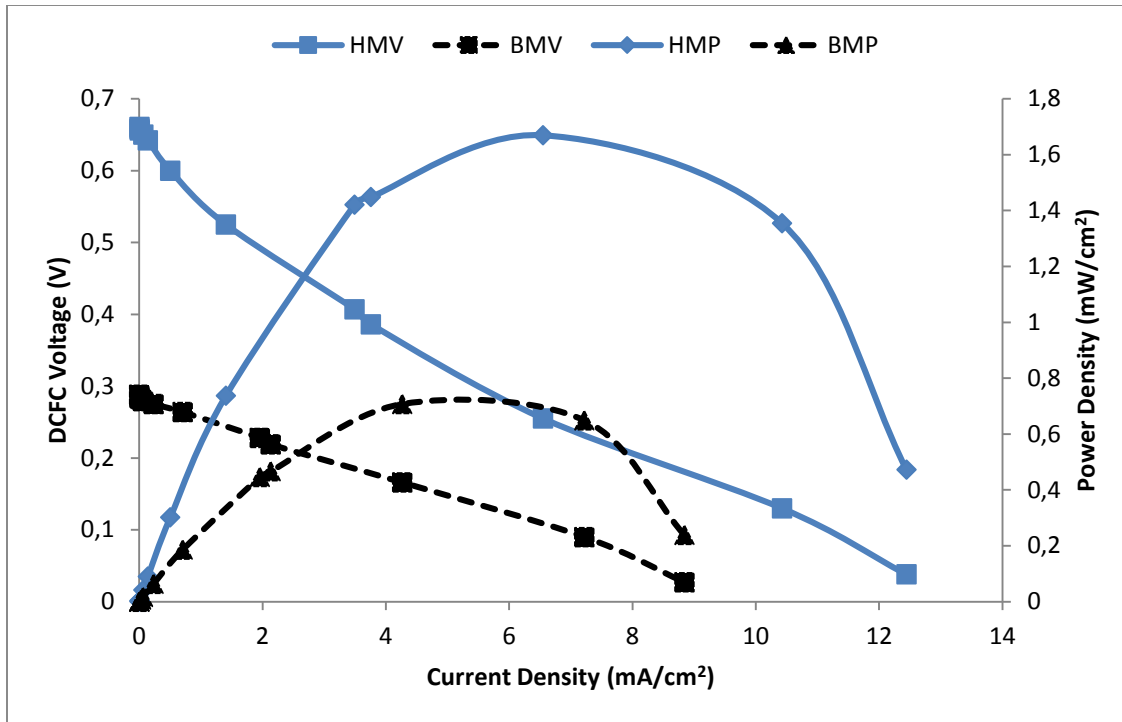


Figure 1 Miscanthus performances for hand (HM) and ball milled (BM) fuels at 600°C.

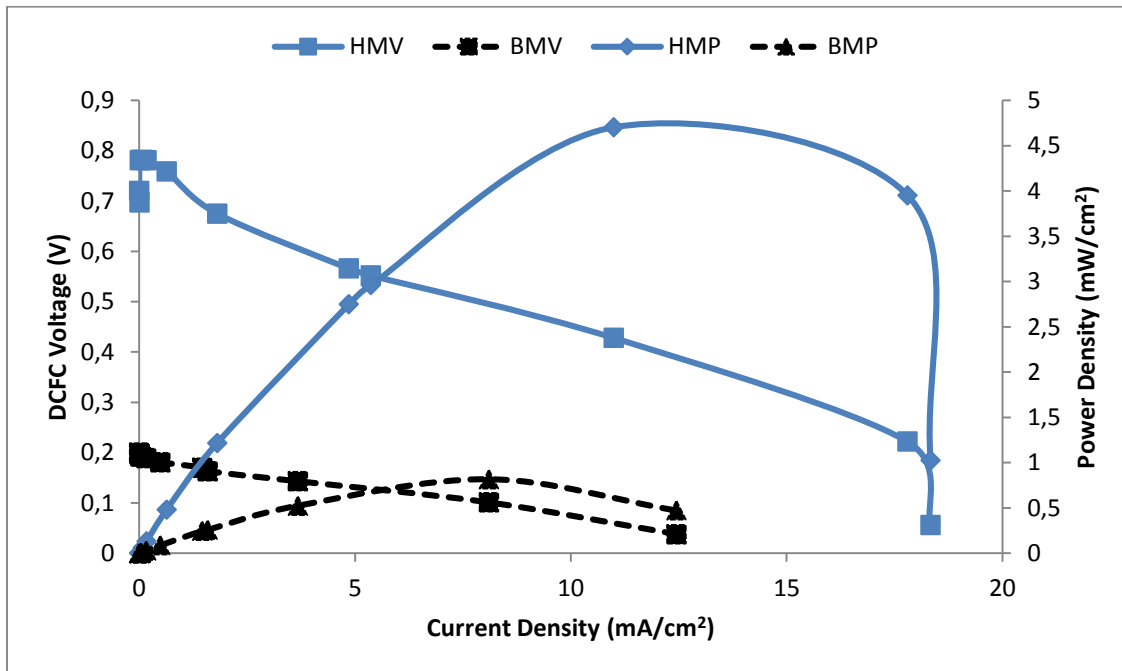


Figure 2 Miscanthus performances for hand and ball milled fuels at 700°C.

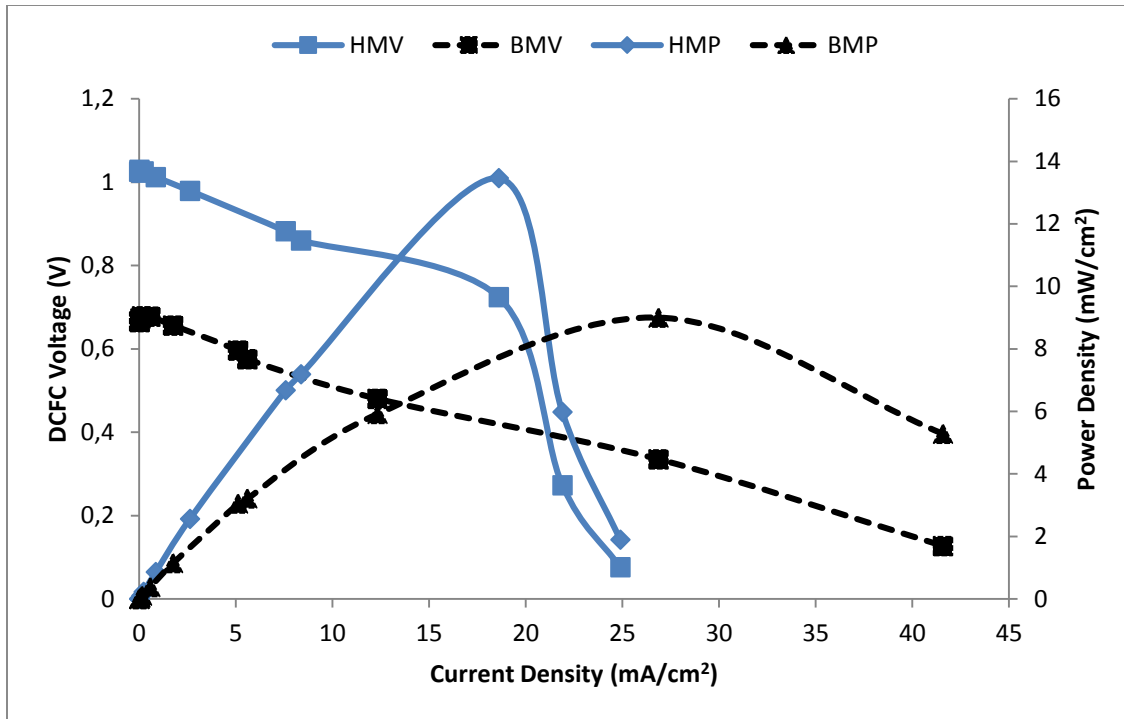


Figure 3 Miscanthus performances for hand and ball milled fuels at 800°C.

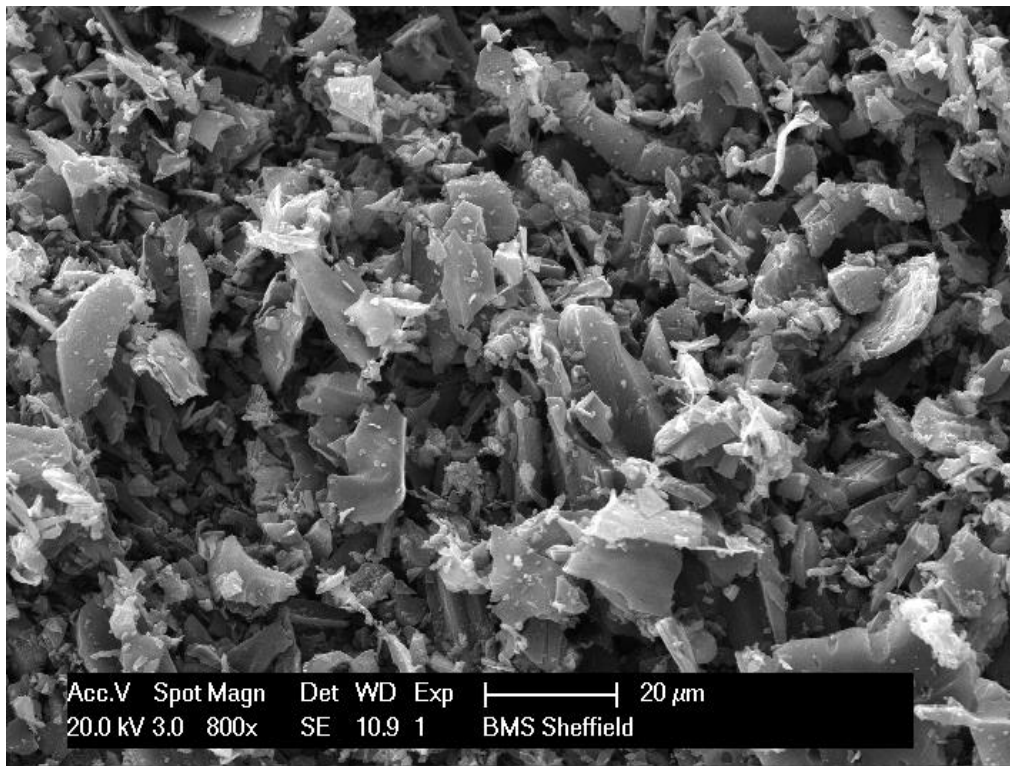


Figure 4 SEM micrograph of hand milled miscanthus carbon particles (800x)

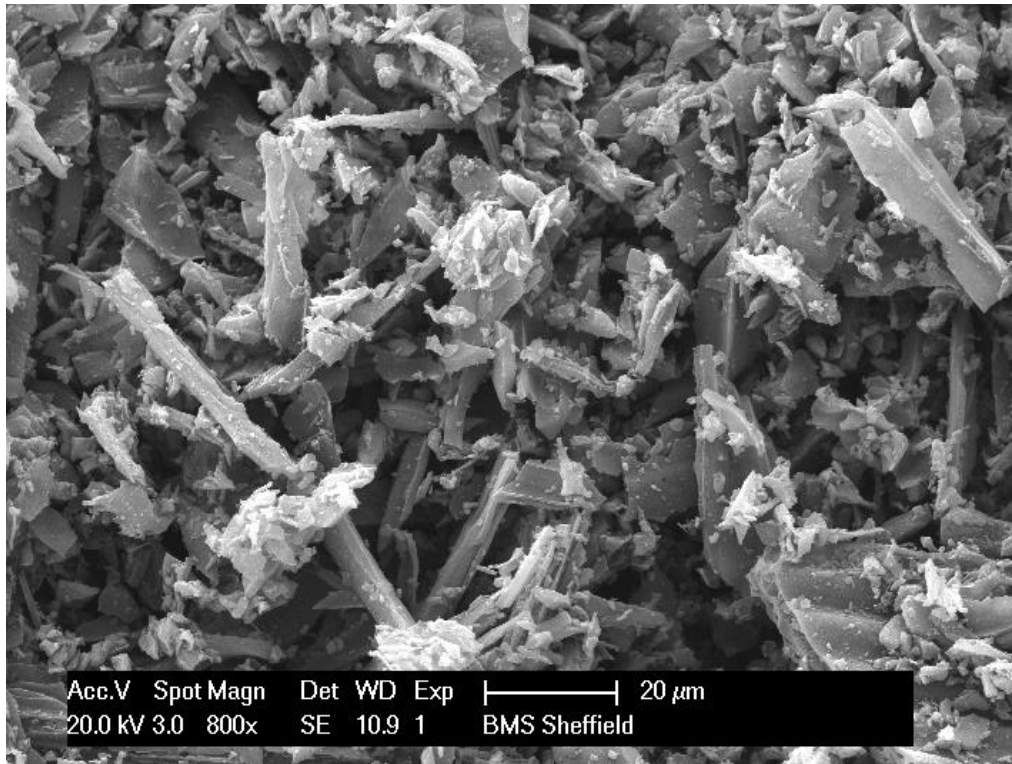


Figure 5 SEM micrograph of ball milled miscanthus carbon particles (800x)

3.2 Switchgrass (*Panicum virgatum*) Carbon Fuel

The difference between the MCDCFC performances using switchgrass HM and BM fuels at 600°C, 700°C and 800°C are shown in Figures 6 to 8. These figures show that the hand milled switchgrass carbon fuels gave better performances than the ball milled. Hand milled carbon fuel has average particle size of 30 μm while the ball milled has 2 μm . Again it was observed that at this particle sizes the effect of milling could not enhance the electrochemical performances. The specific surface area also increased from 0.63 m^2/g for the hand milled to 2.55 m^2/g for the ball milled (Li *et al.*, 2009; Cherepy *et al.*, 2005).

Figures 6 to 8 show that the performances of switchgrass in this case was better than the miscanthus fuel with HM peak power density of 22 mW/cm^2 for switchgrass as against 14 mW/cm^2 for miscanthus at 800°C. Figures 9 and 10 shows the SEM micrographs of the switchgrass carbon fuels. The HM SEM show larger particles than those of the BM as expected but contrary to expectations the hand milled fuel performed better than the ball milled carbon fuels.

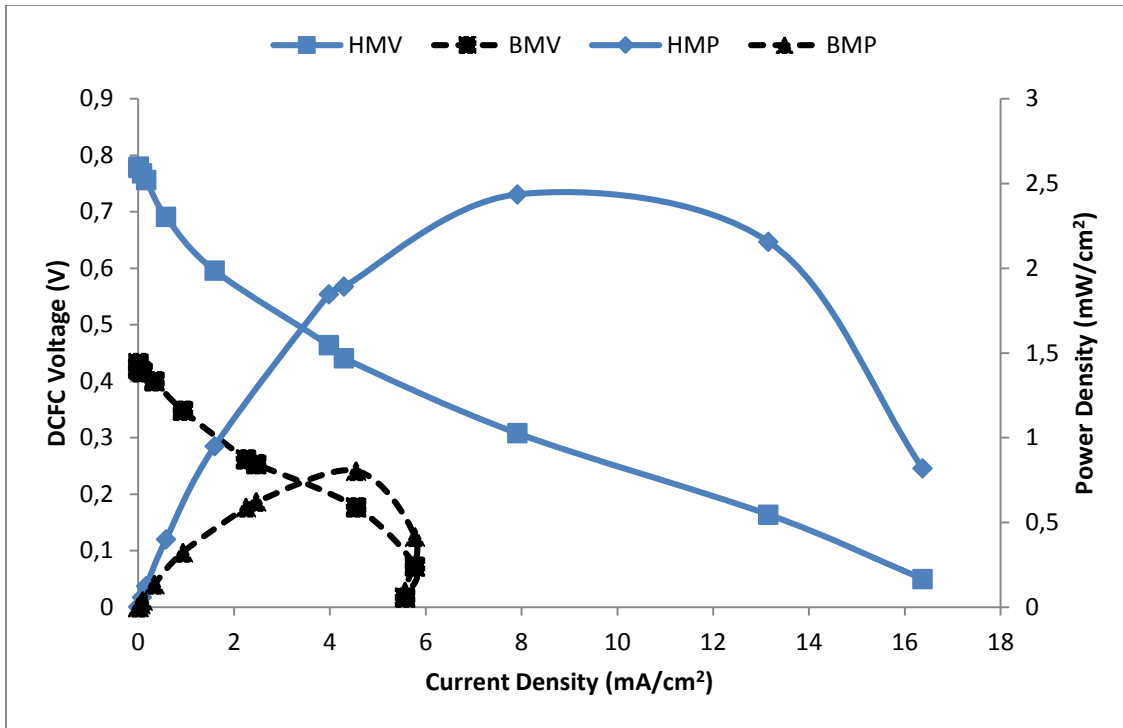


Figure 6 Switchgrass performances for hand and ball milled fuels at 600°C.

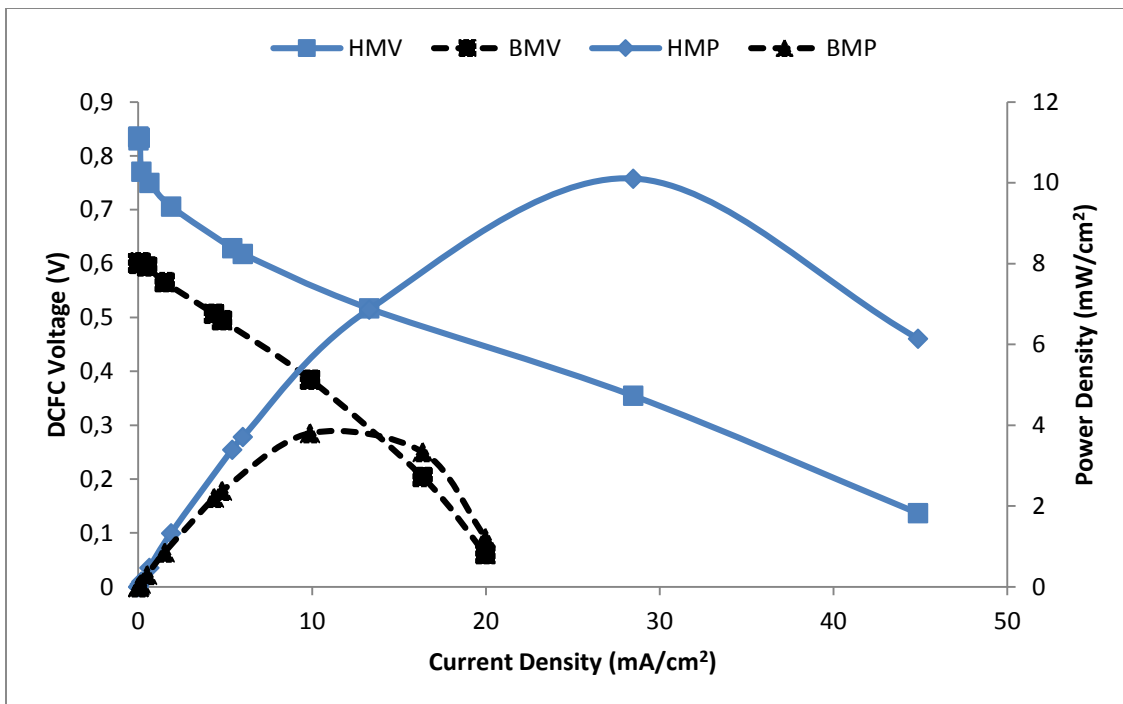


Figure 7 Switchgrass performances for hand and ball milled fuels at 700°C.

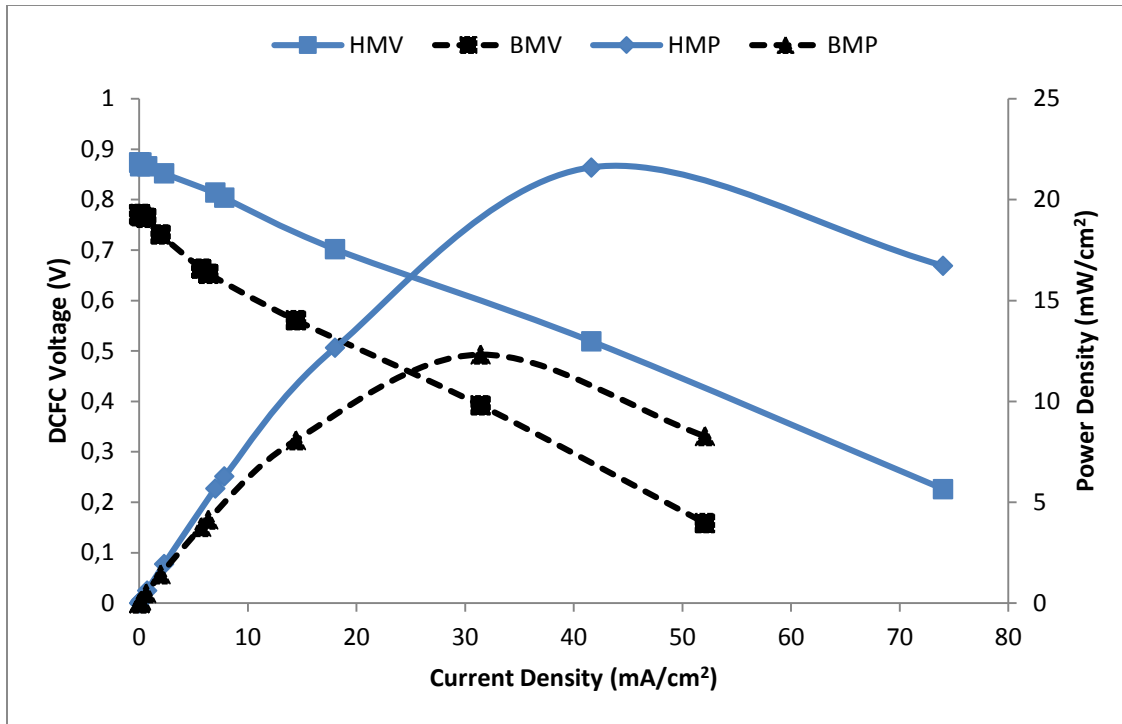


Figure 8 Switchgrass performances for hand and ball milled fuels at 800°C.

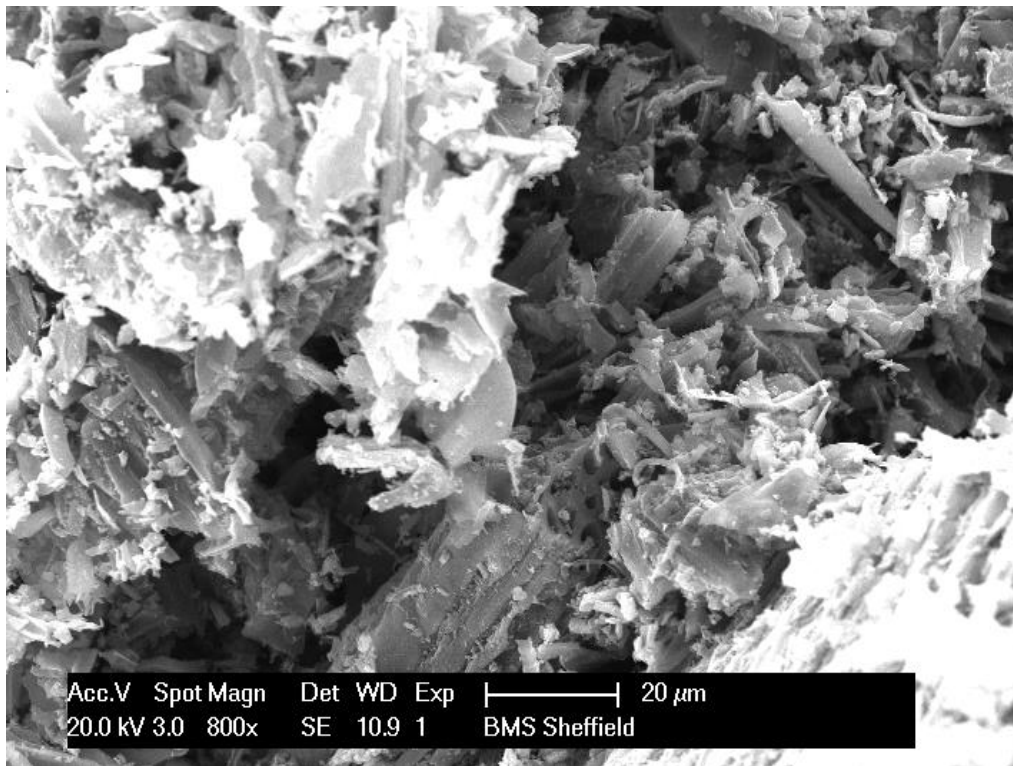


Figure 9 SEM micrograph of hand milled switchgrass carbon particles (800x)

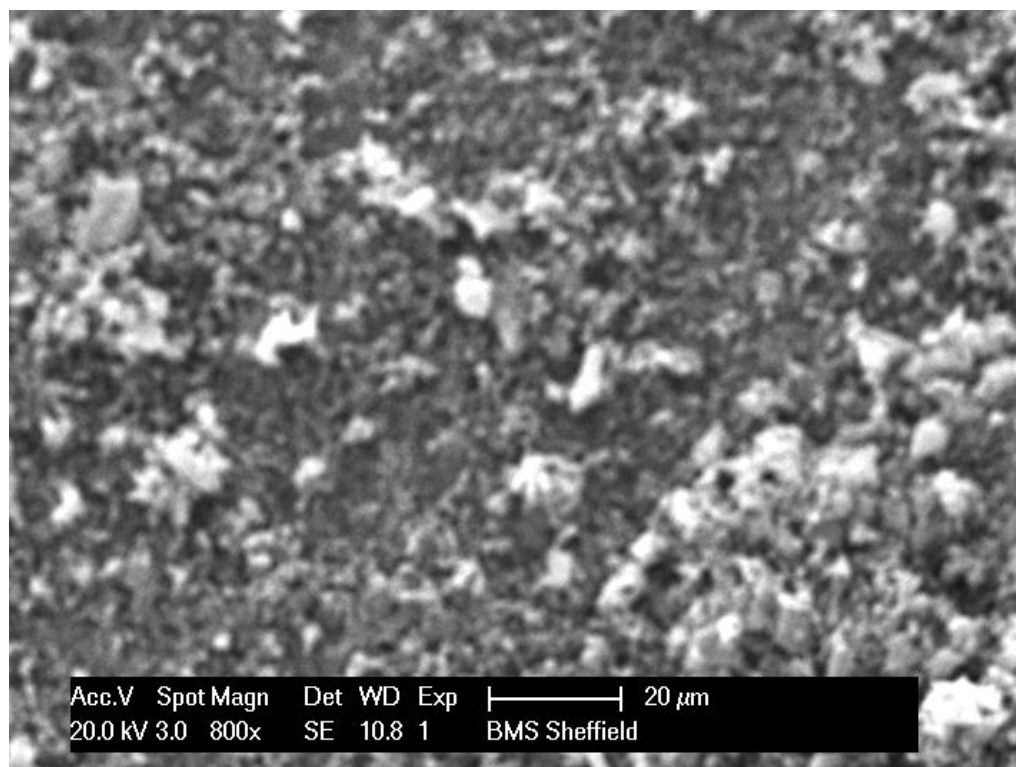


Figure 10 SEM micrograph of ball milled switchgrass carbon particles (800x)

Figures 1 to 3 and 6 to 8 show the characteristics of power and voltage curves behaviour for a single cell molten carbonate electrolyte direct carbon fuel cell (MCDCFC). A number of characteristic electrochemical parameters are presented in Table 1. Miscanthus has the highest power efficiency of 70% at 800°C while switchgrass was lower at 60% at the same operating conditions. The open circuit voltage, peak power density, current density at 80% voltage efficiency and peak power efficiency were all higher for the hand milled carbon fuels.

Table 1 MCDCFC Electrochemical performance at 800°C (HM and BM)

MCDCFC Parameter	Milling type	Miscanthus	Switchgrass
Open circuit voltage (V)	HM	1.03	0.87
	BM	0.67	0.77
Peak power density (mW/cm ²)	HM	13.46	21.60
	BM	9.00	12.32
Maximum current density (mA/cm ²)	HM	24.89	74.00
	BM	41.58	52.06
Current density at 0.8 V (mA/cm ²)	HM	18.59	7.82
	BM	0	0

Voltage at peak power (V)	HM	0.72	0.52
	BM	0.34	0.39
Efficiency at peak power (%)	HM	70.00	60.00
	BM	51.00	51.00

4. CONCLUSIONS

The outcome of a single cell molten carbonate electrolyte direct carbon fuel cell (MCDCFC) electrochemical performances for both the hand (HM) and ball milled (BM) biomass carbon fuels at different operating conditions have been presented. The performances of the hand milled (HM) biomass fuels were higher than those experienced with the ball milled (BM). In terms of the open circuit voltage, miscanthus fuel (1.03 V) has higher values for the HM and switchgrass fuel (0.77 V) for the BM. The best peak power density was recorded for switchgrass fuel (21.60 and 12.32 mW/cm²) for both the HM and BM. Switchgrass fuel (74 mA/cm²) also gave the maximum current density for both the HM and BM. For the current density at 80% voltage efficiency miscanthus fuel (18.59 mA/cm²) was superior for the HM and zero value for the BM for both fuels. Miscanthus fuel (0.72 V) show higher voltage at peak power for the HM and switchgrass fuel (0.39 V) for the BM. The peak power efficiency evaluated show that miscanthus fuel (70%) gave the higher value for the hand milled and equal values for both carbon fuels (51%) for the ball milled.

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Lead Author Bibliography

Dr. Olalekan D. Adeniyi works with the Federal University of Technology Minna, Nigeria. He received his doctorate in energy and environmental engineering from the University of Sheffield, United Kingdom. Over the years, he researched and tutored energy and environmental engineering related courses both at Sheffield and Nigeria.



Dr. Adeniyi has authored over 36 peer-reviewed international and national journal publications. He is a reviewer and editor of several international journals and has attended many national and international conferences. He is a member of numerous professional bodies, like, Nigerian Society of Engineers (NSE), Society of Petroleum Engineers (SPE), Energy Institute (EI), Institution of Chemical Engineers (IChemE), Council for the Regulation of Engineering in Nigeria (COREN), Nigerian Society of Chemical Engineers (NSChE) and others. He is a visiting senior fellow at the School of Petroleum and Chemical Engineering, Covenant University, Ota, Nigeria.