PRODUCTION OF BIOCHAR FROM *MISCANTHUS GIGANTEUS, PANICUM VIRGATUM* AND *ANDROPOGON GAYANUS* FOR A DIRECT CARBON FUEL CELL

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ABSTRACT

Biomass is an important renewable source of energy both in the content of energy change mitigation and energy security. Direct carbon fuel cell with molten carbonate electrolyte (DC-MCDCFC) has attracted growing attention recently as an efficient source of electricity. In this research *miscanthus giganteus, panicum virgatum* and *andropogon gayanus* are used as the raw materials to produce biochar. Pyrolysis condition of heating rate and residence time is held constant at $10^{o}C$/min and 45minutes respectively. A temperature of $700^{o}C$ is used during pyrolysis of each of the three different raw materials, these studies showed that the biochar samples had high carbon content (80.86wt.%, 70.63wt.% and 70.77wt.%), very low sulphur content which is almost negligible, low ash content (18.01wt.%, 28.58wt.% and 27.91wt.%) and the moisture content was very low after pyrolysis (0.30wt.%, 0.25wt.% and 0.35wt.%) for *miscanthus giganteus, panicum virgatum* and *andropogon gayanus* respectively at a produced temperature of $700^{o}C$. However before pyrolysis of the raw materials, the moisture content was very high (3.67wt.%, 3.76wt.% and 4.59wt.%), fixed carbon content was low (8.96wt.%, 15.17wt.% and 10.34wt.%), and the ash content was low (4.91wt.%, 12.01wt.% and 9.78wt.%) for *miscanthus giganteus, panicum virgatum* and *andropogon gayanus* respectively when compared to the result obtained after pyrolysis. Hence the calorific values almost increase twice after pyrolysis (29.97MJ/Kg, 27.96MJ/Kg and 27.99MJ/Kg) when compared to the CV before pyrolysis (15.88MJ/Kg, 17.09MJ/Kg and 16.15MJ/Kg) for *miscanthus giganteus, panicum virgatum* and *andropogon gayanus* respectively. Five different loads resistance (1.0Ω, 1.8Ω, 2.7Ω, 3.9Ω and 4.7Ω) were applied across the cell at an electrochemical reaction temperature region of $450^{o}C$, $500^{o}C$, $550^{o}C$, $600^{o}C$, and $650^{o}C$ respectively. The tests performed with this fuel cell (with active surface area of the cell as $5.73cm^{2}$) showed that all the biochar samples are suitable and attractive fuels for the molten carbonate direct carbon fuel cell (MCDCFC) providing sufficiently high power density. But *miscanthus giganteus* biochar produced at a temperature of $700^{o}C$, held constant at an electrochemical reaction temperature region of $650^{o}C$ in the direct carbon fuel cell (DCFC) have the highest open circuit voltage, current density and power density of 0.63V, $29.67mA/cm^{2}$ and $6.75mW/cm^{2}$ respectively.

Key Words: direct fuel cell, pyrolysis, biochar, biomass, renewable energy, power sources

1.0 INTRODUCTION

The Direct Carbon Fuel Cell (DCFC) uses solid carbon as fuel, for example coal coke, petroleum coke, pyrolysed hydrocarbons, as well as biomass carbon (charcoal) for fuel. Most of the work done in Direct Carbon Fuel Cell (DCFC) uses coal as the carbon anode side of the DCFC. The coal presents the advantage of being the most economic and most abundant fossil resource on the earth (Arizaleta, 2012). But with the advance of biomass carbon (charcoal) for fuel, which has less or no effect to air pollution and climate change mitigation. With this advantages over coal, biomass carbon will be the world leading fuel for electricity generation (Adeniyi *et al.,* 2011).

However, most energy reserves of biomass carbon remain under used and abundant in amounts of greenhouse gasses are produced by convention charcoal fired plants. Improving efficiency in conversion and use of fuel is of chief importance in reducing expenses and pollution, and in prolonging resources (Cao *et al.,* 2007).

A direct carbon fuel cell gives one of the most operative alternatives due to its noticeable higher transformation efficiency (more than double) compared with conventional coal fired power plant (Giddey *et al.,* 2011). Besides, the carbon fuel cell has low CO_2 production rates emissions, when compared with conventional power plants. In principle, the off-gas can be pure carbon-dioxide, which can be directly collected for industrial purpose (Cao *et al.,* 2007) or sequestration leading to substantial cost reductions associated with CO_2 capture and storage. The raw materials for powering a Direct Carbon Fuel Cell (DCFC) are solid, carbon-rich fuels, and much of the effort in recent years has been devoted to fossil fuel carbon sources, such as coal and petroleum coke which eventually leads to air pollution and global warning (Adeniyi *et al.,* 2014).

For a Direct Carbon Fuel Cell (DCFC) power system, both power density and efficiency are critical performance parameters. Power density is critical because it will dictate system size, portability and cost (Cooper *et al.,* 2000). In certain applications, portability and volume requirements may not be primary drivers, but cost is a major concern in any application. Power density serves as a good proxy for cost because the lower the power density, the larger the size of the fuel cell system required to achieve a given power output (Weaver *et al.,* 1979). Manufacturing and material costs scale with fuel cell size; thus, the larger the fuel cell system becomes, the greater the material and manufacturing costs will be. Efficiency is critical because it is the key metric that differentiates Direct Carbon Fuel Cell (DCFC) from other technologies. Direct Carbon Fuel Cell (DCFC) has the potential to far exceed the efficiencies of other technologies, including other fuel cells. However, if this efficiency cannot be achieved, then the Direct Carbon Fuel Cell (DCFC) will likely not be competitive with other fuel cell options due to the lower power density and larger size of the Direct Carbon Fuel Cell (DCFC) (Perwich *et al.,* 2012).

The Direct Carbon Fuel Cell (DCFC) is becoming more important because of the various advantages that it offers. Because no heat engines or reformers are needed in the Direct Carbon Fuel Cell (DCFC) system it is mechanically simple to build and can be located around biomass sites, thus reducing the cost of transportation, and reducing environmental pollution. The production of tiny carbon particles produced by pyrolysis and used in the Direct Carbon Fuel Cell (DCFC) requires less energy and capital than the production of hydrogen-rich fuels used in other fuel cell types. Since carbon oxidation is achieved electrochemically at the anode without direct mixing with air, the CO_2 is created as a pure gas which can be captured and stored as part of a carbon capture and storage (CCS) strategy (Adeniyi *et al.,* 2014).

3.0 Materials and methods

3.1 Materials

All materials for the production process were gotten from FUTMinna and those for analysis were gotten from Kaduna research centres.

3.2 Methods

The methods for production, pyrolisis and analysis are standard procedures for biochar as described by (Adeniyi et al., 2014).

4.0 RESULT AND DISCUSSION

4.1 Biomass Analyses

Table 4.1 shows the result of proximate analysis, ultimate analysis and the calorific value (CV) of ground *miscanthus giganteus, panicum virgatum* and *andropogon gayanus* before pyrolysis. The proximate analysis constitute the moisture content, ash content, fixed carbon and volatile content. The moisture content of the biomass varies between 3.67 wt.% to 4.59 wt.%, with the minimum value in *miscanthus giganteus* and the maximum in *andropogon gayanus*. This shows that all the samples were stored, processed well before being collected. The ash content varies more than the moisture content, it values ranges between 9.78 wt.% to 12.01

wt.%, *panicum virgatum* gives maximum value of 12.01wt.% ash content while *miscanthus giganteus* have minimum value of 4.91 wt.% of ash content.

Further results shows that the volatile matter has very narrow range, that is between 69.06 wt.% to 82.46 wt.% with *miscanthus giganteus* having the maximum volatile content of 82.46 wt.% and *panicum virgatum* having the minimum volatile matter of 69.06 wt.%. The fixed carbon content also varies slightly between the three given samples, between the ranges of 8.96 wt.% to 15.17 wt.%, with *miscanthus giganteus* having the minimum fixed carbon content of 8.96 wt.% and *panicum virgatum* having the maximum value of 15.17 wt.% of fixed carbon content.

Ultimate analysis this constitutes the carbon, hydrogen, oxygen, sulphur and nitrogen present in the samples. The ultimate analysis values for all the three samples as shown in table 4.1 indicates that carbon has the highest values when compared with the rest followed by oxygen after which hydrogen is next which lies within the ranges of 4.03 wt.% to 12.70 wt.%. The content of sulphur and nitrogen are very small so they are nearly negligible in all the samples and lies between the ranges of 0.01 wt.% to 0.46 wt.% for all the samples. *miscanthus giganteus* is found to be more useful due to its high carbon of 52.01 wt.% when compared to other biomasses used.

Calorific value in MJ/Kg for the samples are in a very narrow close range between 15.88 MJ/Kg to 17.09 MJ/Kg with the maximum calorific value in *panicum virgatum* and the minimum in *miscanthus giganteus* with the values of 17.09 MJ/Kg and 15.88 MJ/Kg respectively.

Table (4.1): Proximate, ultimate and calorific value analysis of ground *miscanthus g., panicum v.* and

Analysis	Proximate Analysis				Calorific Value (MJ/Kg)	Ultimate Analysis				
Biomass	Moisture content Wt. %	Ash content Wt.%	Fixed carbon Wt. %	Volatile content Wt. %		Carbon Wt. %	Hydrogen Wt. %	Oxygen Wt. %	Nitrogen Wt. %	Sulphur Wt. %
miscanthus g.	3.67	4.91	8.96	82.46	15.88	52.01	4.03	43.87	0.06	0.03
Panicum v.	3.76	12.01	15.17	69.06	17.09	49.92	8.66	41.13	0.21	0.08
Andropogon g.	4.59	9.78	10.34	75.28	16.15	50.11	12.70	36.72	0.46	0.01

andropogon g.

4.2 Pyrolysis and Carbon Analyses

The result of analysis carried out for the three different samples of biochars produced through pyrolysis at 700°C is presented on table 3.2. The moisture content lies in a very close narrow range of 0.25wt.% to 0.35wt.% with *panicum* grass biochar produced at 700°C having the minimum value of 0.25wt.% and *andropogon* grasses biochar produced at 700°C having the maximum value of 0.35wt.%. The ash content varies more than the moisture content. It values ranges between 18.01wt.% to 28.58wt.% with *panicum* grass biochar having the maximum value of 28.58wt.% and *miscanthus* biochar having the minimum value of 18.01wt.% of ash content. Hydrogen content fall in the range of 0.54wt.% to 0.97wt.% while the carbon content lies between 70.63wt.% to 80.86wt.% with the highest value of carbon content found in *miscanthus* biochar and the lowest in *panicum* grass biochar. The calorific value falls in a range of 27.96MJ/Kg to 29.97MJ/Kg with *miscanthus* biochar having the maximum value and *panicum* grass biochar having the minimum calorific value (CV).

On comparing the analysis carried out for the ground biomasses on table 3.1 and the analysis of the biochar produced at 700°C on table 3.2. For *miscanthus, panicum* grass, and *andropogon* grasses the moisture content from the ground to the biochar reduced from 3.67 wt.% to 0.30 wt.%, 3.76 wt.% to 0.25 wt.%, and 4.59 wt.% to 0.35 wt.% respectively (Tables 3.1 and 3.2). the ash content from the ground to the biochar increases from 4.91 wt.% to 18.01 wt.%, 12.01 wt.% to 28.58 wt.%, and 9.78 wt.% to 27.91 wt.% respectively (Tables 3.1 and 3.2). The calorific value has greatly improved from 15.88 MJ/kg to 29.97MJ/Kg, 17.09 MJ/kg to 27.96 MJ/kg, 16.15 MJ/kg to 27.99 MJ/kg for *miscanthus, panicum* grass, and *andropogon* grasses respectively (Tables 3.1 and 3.2). The carbon content almost double from 52.01 wt.% to 80.86 wt.%, 49.92 wt.% to 70.63 wt.%, and 50.11

wt.% to 70.77 wt.% for *miscanthus, panicum* grass, and *andropogon* grasses respectively (Tables 3.1 and 3.2) and the hydrogen content reduced from 4.03 wt.% to 0.83 wt.%, 8.66 wt.% to 0.54 wt.%, and 12.70 wt.% to 0.97 wt.% for *miscanthus*, *panicum* grass, and *andropogon* grasses respectively (Tables 3.1 and 3.2). From Table 3.2, *miscanthus* biochar (29.97 MJ/kg) has the highest calorific value followed by *panicum* grasses biochar (27.99 MJ/kg), then *panicum* grass biochar (27.96 MJ/kg), although there is just a little difference between the calorific value of andropogon grasses and *panicum* grass. These heating values will have effects on the performance of the biomass fuel in the fuel cells. Also similar patterns were observed in the carbon contents of these carbon fuels.

Table (4.2): Moisture, ash, calorific value and ultimate analyses of bio-char from *miscanthus, panicum,* and *andropogon* grasses produced at 700°C

Biochar	Moisture content wt.%	Ash content wt.%	Calorific value MJ/Kg	Carbon wt.%	Hydrogen wt.%
Miscanthus	0.30	18.01	29.97	80.86	0.83
panicun	0.25	28.58	27.96	70.63	0.54
adropogogon	0.35	27.91	27.99	70.77	0.97

3.3 Effect of Electrochemical Reaction Temperature on Biochar.

3.4 Molten Carbonate Direct Carbon Fuel Cell (MCDCFC) Performances using *Miscanthus* Biochar Fuel Produced at a Temperature of 700°C

Figure 4.1 shows the result obtained from the molten carbonate direct carbon fuel cell (MCDCFC), using *miscanthus* biochar fuel produced at a temperature of 700°C at five different electrochemical reaction temperature regions of 650°C, 600°C, 550°C, 500°C, and 450°C respectively.

The result obtained from the graph shows that at the lowest electrochemical reaction temperature of 450°C the open circuit voltage (OCV) of 0.47V was obtained having the current density of 19.20mA/cm^2, at 500°C a voltage of 0.52V with a maximum current density of 22.69mA/cm^2, at 550°C a voltage of 0.58V with a maximum current density of 22.69mA/cm^2 at this point there is increase in voltage as the electrochemical reaction temperature regions were increased. At 600°C the values obtained for OCV and current density were 0.62V and 26.18mA/cm^2 respectively. Then finally at the highest electrochemical reaction temperature region of 650°C the highest OCV and maximum current density values were obtained as 0.63V and 29.67mA/cm^2 respectively.

At a constant electrochemical reaction temperature the corresponding drops in the voltages was as a result of the load (resistance) applied to the cell. As the resistance (load) is reduce the voltage drops and the current increases. Five different load (resistance) were applied 4.7, 3.9, 2.7, 1.8 and 1.0 ohms resistors were applied across the cell at a constant electrochemical reaction temperature region. As the electrochemical reaction temperature increases the maximum current density increases, which indicates that at a very high electrochemical reaction temperature region a high current density will be achieved.

At an electrochemical reaction temperature region of 450°C, 500°C, and 550°C, the voltage falls rapidly due to activation resistance. This activation resistance leads to activation polarization (losses) which shows that the reaction kinetics on the electrode are slow, while at an electrochemical reaction temperature region of 600°C and 650°C the voltage drops slowly which indicates that the reaction kinetics on the electrodes are fast when compared to the electrochemical reaction temperature regions at 450°C, 500°C and 550°C. The voltage generated is lost in driving the chemical reaction that transfers the electrons to and from the electrodes.

At both electrochemical reaction temperature regions (that is 650°C, 600°C, 550°C, 500°C, and 450°C) the curves continue to decrease linearly due to ohmic resistance of the fuel cell and this ohmic resistance (load) leads to ohmic polarization (losses), which are due to resistance offered to the flow of electrons and ions through the electrode and electrolyte respectively. The fuel cell consist of electrodes and electrolyte, electrodes offers resistance to the flow of electrons, where as the electrolyte provide obstruction to the flow of ions. This occurs due to the flow of electrons at the anode sides of the fuel cell through the electrolytes.

However the voltage falls faster at high current density due to mass transport or concentration polarization (losses). This is as a result of change in concentration of the reactants at the surface of the electrode as the biochar fuel is being consumed in the cell. The reduction in the concentration leads to insufficient reactions

transportation to the electrode surface or otherwise known as mass transport losses (Li *et al.,* 2010, Adeniyi *et al.,* 2014, Zhao *et al.,* 2010, Kacprzak *et al.,* 2013, Rasul *et al.,* 2013, Cooper *et al.,* 2007).

The power densities versus current densities for *miscanthus* biochar produced at a temperature of 700°C using five different electrochemical reaction temperature regions that is 650°C, 600°C, 550°C, 500°C and 450°C. The graph shows that there was an increase in the power densities and current densities with the increase in electrochemical reaction temperature, the highest power density was recorded at 650°C (6.35WA/cm^2) at the maximum current density of 29.67mA/cm^2, at an electrochemical reaction temperature region of 600°C the maximum power density was 5.02mW/cm^2 at a maximum current density of 26.18mA/cm^2, at 550°C the maximum power density was 3.79mW/cm^2 and the maximum current density was 22.69mA/cm^2, at 500°C the maximum power density was 3.26mW/cm^2 with a current density of 22.69mA/cm^2 and it greatly reduce at 450°C the maximum power density of 2.37mW/cm^2 was achieved at a maximum current density of 19.19mA/cm^2.
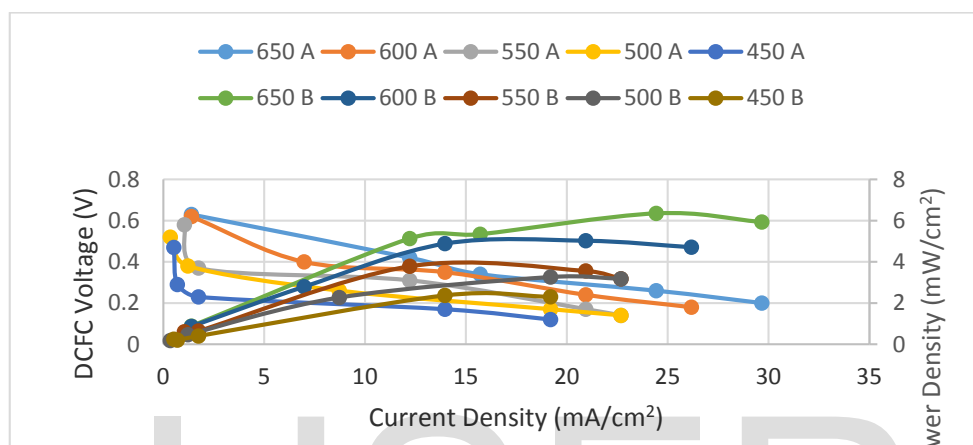

Figure (4.1): Voltage, power versus current density using *miscanthus* biochar produced at 700°C at different electrochemical reaction temperature.

4.3 Molten Carbonate Direct Carbon Fuel Cell (MCDCFC) Performances using *Panicum* Biochar produced at a Temperature of 700°C

Figure 3.2 shows the result obtained from the molten carbonate direct carbon fuel cell (MCDCFC), using *panicum* grass biochar produced at a temperature of 700°C at five different electrochemical reaction temperature regions of 650°C, 600°C, 550°C, 500°C, and 450°C respectively.

The result obtained from the graph shows that at the lowest electrochemical reaction temperature of 450°C the open circuit voltage (OCV) of 0.38V was obtained having the current density of 13.96mA/cm^2, at 500°C a voltage of 0.38V with a maximum current density of 13.96mA/cm^2, at 550°C a voltage of 0.44V with a maximum current density of 19.20mA/cm^2. At 600°C the values obtained for OCV and current density were 0.50V and 20.94mA/cm^2 respectively. Then finally at the highest electrochemical reaction temperature region of 650°C the highest OCV and maximum current density values were obtained as 0.55V and 26.18mA/cm^2 respectively.

At a constant electrochemical reaction temperature region the corresponding drops in the voltages was as a result of the load (resistance) applied to the cell. As the resistance (load) is reduce the voltage drops and the current increases. Five different loads (resistance) were applied across the cell at a constant electrochemical reaction temperature region. As the electrochemical reaction temperature increases the maximum current density increases, which indicates that at a very high electrochemical reaction temperature region a high current density will be achieved.

In figure 3.2 at electrochemical reaction temperature regions of 450°C, 500°C, 550°C and 600°C, the voltage falls rapidly due to activation resistance. This activation resistance leads to activation polarization (losses) which shows that the reaction kinetics on the electrode are slow, while at an electrochemical reaction temperature region of 650°C the voltage drops slowly which indicates that the reaction kinetics on the electrodes are fast

when compared to the electrochemical reaction temperature regions at 450°C, 500°C 550°C and 600°C. The voltage generated is lost in driving the chemical reaction that transfers the electrons to and from the electrodes.

At both electrochemical reactions temperature regions the curves continue to decrease linearly due to ohmic resistance of the fuel cell and this ohmic resistance (load) leads to ohmic polarization (losses), which are due to resistance offered to the flow of electrons and ions through the electrode and electrolyte respectively. The fuel cell consist of electrodes and electrolyte, electrodes offers resistance to the flow of electrons, where as the electrolyte provide obstruction to the flow of ions. This occurs due to the flow of electrons at the anode sides of the fuel cell through the electrolytes.

However the voltage falls faster in the electrochemical reaction temperature region of 500°C when compared to order electrochemical reaction temperature regions at high current density due to mass transport or concentration polarization (losses). This is as a result of change in concentration of the reactants at the surface of the electrode as the biomass fuel is being consumed in the cell. The reduction in the concentration leads to insufficient reactions transportation to the electrode surface or otherwise known as mass transport losses (Li *et al.,* 2010, Adeniyi *et al.,* 2014, Zhao *et al.,* 2010, Kacprzak *et al.,* 2013).

Figure 3.2 shows the power densities versus current densities for *panicum* grass biochars produced at a temperature of 700°C using five different electrochemical reaction temperature regions that is 650°C, 600°C, 550°C, 500°C and 450°C. The graph shows that there was increase in the power densities and current densities with the increase in electrochemical reaction temperature, the highest power density was recorded at 650°C (5.03mW/cm^2) at the maximum current density of 26.18mA/cm^2, at a electrochemical reaction temperature region of 600°C the maximum power density was 3.32mW/cm^2 at a maximum current density of 20.94mA/cm^2, at 550°C the maximum power density was 2.69mW/cm^2 and the maximum current density was 19.20mA/cm^2, at 500°C the maximum power density was 2.20mW/cm^2 with a current density of 13.96mA/cm^2 and it reduce at 450°C the maximum power density of 1.33mW/cm^2 was achieved at a maximum current density of 13.96mA/cm^2.

Figure (4.2): Voltage, power versus current density using *panicum* grass biomass produced at 700°C at different electrochemical reaction temperature.

In general, in comparing the results obtained for switch grass biochars produced at a temperature of 700°C, with *miscanthus* biomass produced at a temperature of 700°C. It was observed that there is a very rapid fall in voltage for the three different electrochemical reaction temperature (550°C, 500°C and 450°C) in *miscanthus* biochar. However, in *panicum* grass biochar, the falls in voltage are in four different electrochemical reaction temperature regions (600°C, 550°C, 500°C and 450°C) which are due to activation resistance (losses). On the same graph at a very high current density, there was a sharp drop at the electrochemical reaction temperature region of 500°C for *panicum* grass biochar produced at 700°C. There is a high current density and high power density in *miscanthus* biochar when compared to *panicum* grass biochar. The drop in voltage in *panicum* grass biochar was high when compared to *miscanthus* biochar.

4.4 Molten Carbonate Direct Carbon Fuel Cell (MCDCFC) Performance using *andropogon* grasses Biochar Produced at 700°C.

Figure 4.3 shows the result obtained from the molten carbonate direct carbon   fuel cell (MCDCFC), using andropogon grasses biochar produced at a temperature of 700°C. The result obtained from the graph shows that at the lowest electrochemical reaction temperature of 450°C the open circuit voltage (OCV) of 0.31V was obtained having the current density of 3.49mA/cm^2, at 500°C a voltage of 0.36V with a maximum current density of 5.24mA/cm^2, at 550°C a voltage of 0.41V with a maximum current density of 13.96mA/cm^2. At 600°C the values obtained for OCV and current density were 0.48V and 13.96mA/cm^2 respectively. Then finally at the highest electrochemical reaction temperature region of 650°C the highest OCV and maximum current density values were obtained as 0.48V and 20.94mA/cm^2 respectively.

At a constant electrochemical reaction temperature the corresponding drops in the voltages was as a result of the load (resistance) applied to the cell. As the resistance (load) is reduce the voltage drops and the current increases. Five different loads (resistance) across the cell were applied, at a constant electrochemical reaction temperature region. As the electrochemical reaction temperature increases the maximum current density increases, which indicates that at a very high electrochemical reaction temperature region a high current density will be achieved.

In figure 3.3 the electrochemical reaction temperature regions of the voltage falls rapidly due to activation resistance. This activation resistance leads to activation polarization (losses) which shows that the reaction kinetics on the electrode is slow in all the electrochemical reaction temperature regions. The voltage generated is lost in driving the chemical reaction that transfers the electrons to and from the electrodes.

At both electrochemical reaction temperature regions (that is 650°C, 600°C, 550°C, 500°C, and 450°C) the curves continue to decrease linearly due to ohmic resistance of the fuel cell and this ohmic resistance (load) leads to ohmic polarization (losses), which are due to resistance offered to the flow of electrons and ions through the electrode and electrolyte respectively.

However the voltage falls faster at high current density due to mass transport or concentration polarization (losses) in 650°C, 600°C, 550°C electrochemical reaction temperature regions. This is as a result of change in concentration of the reactants at the surface of the electrode as the biomass fuel is being consumed in the cell. The reduction in the concentration leads to insufficient reactions transportation to the electrode surface or otherwise known as mass transport losses (Li *et al.,* 2010, Adeniyi *et al.,* 2014, Zhao *et al.,* 2010, Kacprzak *et al.,* 2013).   At a low current density there observed a sharp falls in voltage at a electrochemical reaction temperature regions of 450°Cand 500°C.

Figure 3.3 shows the power densities and current densities for andropogon grass biochar produced at a temperature of 700°C using five different electrochemical reaction temperature regions that is 650°C, 600°C, 550°C, 500°C and 450°C. The graph shows that there was increase in the power densities and current densities with the increase in electrochemical reaction temperature, the highest power density was recorded at 650°C (4.19mW/cm^2) at the maximum current density of 20.94mA/cm^2, at a electrochemical reaction temperature region of 600°C the maximum power density was 2.41mW/cm^2 at a maximum current density of 13.96mA/cm^2, at 550°C the maximum power density was 2.44mW/cm^2 and the maximum current density was 13.96mA/cm^2, at 500°C the maximum power density was 0.73mW/cm^2 with a current density of 5.24mA/cm^2 and it reduce at 450°C   the maximum power density of 0.26mW/cm^2 was achieved at a maximum current density of 3.49mA/cm^2.
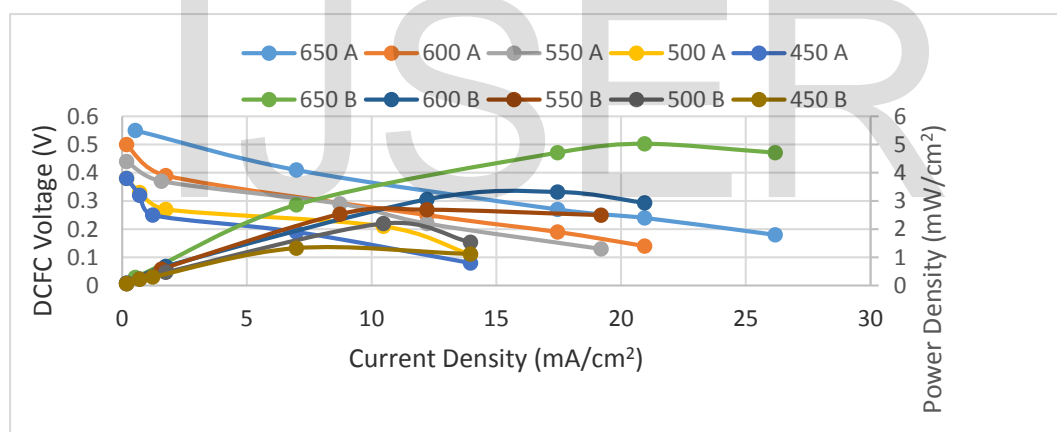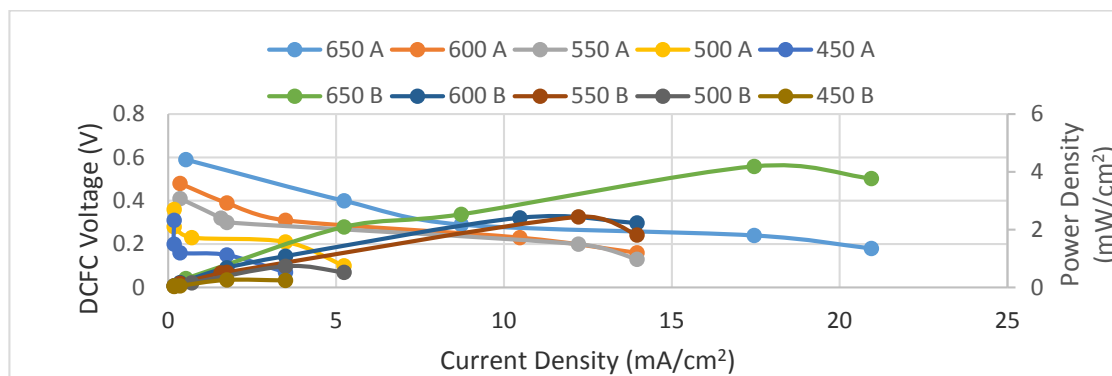

Figure (4.4): Voltage, power versus current density using *andropogon* grasses biochar produced at 700°C at different electrochemical reaction temperature.

The results indicate that the increase in the electrochemical reaction temperature brings about increase of the electrical parameters of the cell. One of the reasons that the fuel cell generate high power density and current density was probably the improve conductivity of the electrolyte, in addition to increase in the reaction rate. The increase in electrochemical reaction temperature not only improves the performance of the cell, but also has an impact on the corrosion that will lead to the subsequent shut down of the fuel cell.

In general, the voltage drop in *andropogon* grasses biochar was high when compared to *panicum* grass biochar and the voltage drop in *panicum* grass biochar was higher when compared to *miscanthus* biochar. However the graph for *miscanthus* biochar was linear when compared to *panicum* grass and *andropogon* grasses biochar. More so, at a low operating electrochemical reaction temperature the drop in voltage for *miscanthus* biochar was fair when compared to *panicum* grass and *andropogon* grasses biochar.

Performance Testing Setup of the DCFC

Figures show the complete direct carbon fuel cell (DCFC) stand, showing the digital thermocouple, resistor box, voltmeter, furnace in which the direct carbon fuel cell (DCFC) was heated and the various connections for the gases. With all these in their right places and in order to prevent any rapid expansion of the cell, the furnace was heated up gradually at $10^{o}C$/min. When the MCDCFC temperature was at $250^{o}C$, nitrogen gas was introduced through the anode at a rate of 200 cm^3/min to purge it, throughout the measurement. At a temperature of $350^{o}C$ the air (Oxygen gas) was released through the cathode at a rate of 1500 cm^3/min, throughout the experiment (Adeniyi, 2014). The DCFC was heated up to an electrochemical reaction temperature of $800^{o}C$ while measuring the voltage outputs. After the measurement, the furnace was shut down with nitrogen gas running till $300^{o}C$ (Adeniyi, 2014). Five different resistances were used (1.0 Ω to 4.7 Ω), the open circuit voltage was taken at the highest resistance. The switch on the box was turned to the next resistance while allowing the voltage to settle down and the reading taken. This was repeated each time for all the resistances and the voltages taken.

The simple mechanisms that are involved in the generation of electrons are; the direct carbon fuel cell basically comprises of the anode and the cathode side, separated by an electronically insolating and ionically conducting electrolyte, however the anode side is been supplied with nitrogen gas and the cathode side been supplied with oxygen gas. The oxygen gas that is passed through the cathode side of the DCFC ionised and ions migrate through the electrolyte to the anode side. The ions combine with the fuel to produce electrons. The electrons travel around a circuit through a load to the cathode side. At the cathode side electrons combine with O_2 producing ions, the process repeats for as long as fuel and oxidant are supplied.

However the electrolyte is an ion conductor only that is it does not conduct electrons. In summary on the cathode side, O_2 is reduced to oxide ions (O^{2-}) consuming two electrons and on the anode side the ions combine with the fuel releasing two electrons.

Plate (1): Performance Testing Setup of the DCFC

Figure (1): Direct Carbon Fuel Cell (DCFC) and its specifications

Plate (2): Direct Carbon Fuel Cell (DCFC)

5.1 Conclusions

The material characterisation of the three biomasses investigated indicates that they consist of different compositions. The proximate analysis reveals that they have different moisture content, ash content, volatiles content and fixed carbon content. While the ultimate analysis shows that they also have different carbon and hydrogen content. These studies showed that before pyrolysis the moisture content was very low, it contains a little ash, no mercury, almost no sulphur and the nitrogen content is very negligible. On the basis of proximate analysis of the three biomass samples before pyrolysis *miscanthus* is found to be most useful because of its high carbon content. However after pyrolysis of each of the biomasses at different temperature also reveals that there material characterisation are different. Pyrolysis reaction greatly enhanced the properties of the biomass carbon produced. The result obtained shows that there were increase in carbon content, calorific value, reduce in moisture content and hydrogen content composition for all the samples produced at different temperatures. This result obtained were within the recorded values from literatures (Li *et al.,* 2010, Adeniyi *et al.,* 2014, Zhao *et al.,* 2010, Kacprzak *et al.,* 2013, Rasul *et al.,* 2012).

The performances of biochar fuels were tested in a single cell MCDCFC using the same electrochemical cell arrangement. For *miscanthus* produced at $700^{o}C$ at the maximum electrochemical reaction temperature region of $650^{o}C$ gives the OCV of 0.63V, maximum current of 29.7mA/cm^2 and peak power density of 6.4mW/cm^2, for switch grass produced at $700^{o}C$ at the maximum electrochemical reaction temperature region of $650^{o}C$ gives the OCV of 0.55V, maximum current of 26.2mA/cm^2 and peak power density of 5.03mW/cm^2, for *andropogon* grsses produced at $700^{o}C$ at the maximum electrochemical reaction temperature region of $650^{o}C$ gives the OCV of 0.59V, maximum current of 20.9mA/cm^2 and peak power density of 4.19mW/cm^2. However for *miscanthus* produced at $700^{o}C$ at the maximum electrochemical reaction temperature region of $650^{o}C$ gives the maximum

OCV, current density and power density of 0.63V, 29.7mA/cm^2 and 6.4mW/cm^2 respectively. This implies that temperature as great effect on the pyrolysis of biomasses and the electrochemical reaction temperature also have great effect on the performance testing of the biochar samples.

REFERENCES

1. Bruce, C. R. E., and Adeniyi O.D., (2013). A Demonstration of Carbon-Assisted Water Electrolysis. Journal of Energies, 6, 1657-1668; doi: 10.3390/en6031657.
2. Adeniyi O.D., Bruce C.R. E., Mary I. A., Mukhtar A. (2014). The Behaviour of Biomass Char in Two Direct Carbon Fuel Cell Designs. Journal of energy challenges and mechanics, Volume 1 issue 4, article 6.
3. Rasul, M. G., Jahirul, M. I., Chowdhury, A. A., and Ashwath, N. (2012). Biofuels Production through Biomass Pyrolysis-A Technological Review. Journal of Energies, 5, 4952-5001; doi:10.3390/en5124952.
4. Cao, D., Sun, Y., Wang, G. (2007). Direct carbon fuel cell: Fundamentals and recent developments. J. Power Sources, 167, 250–257.
5. Adeniyi, O. D., Ewan, C. R., Adeniyi, M. I., and Abdulkadir, M. (2014). The Behaviour of Biomass Char in Two Direct Carbon Fuel Cell Designs. Journal of Energy Challenges and Mechanics, Volume 1, Issue 4, article 6, 2056-9386. Retrieved from http://www.nscj.co.uk/JECM/.
6. Zhao, X., Song, Z., Liu, H., Li, Z., Li, L., Ma, C. (2010) Microwave pyrolysis of corn stalk bale: A promising method for direct utilization of large-sized biomass and syngas production. J. Anal. Appl. Pyrolysis, 89, 87–94.
7. Li, X., Zhu, Z., de Marco, R., Bradley, J., Dicks, A. (2010). Evaluation of raw coals as fuel for direct carbon fuel cells. J. Power Sources, 195, 4051–4058.
8. McKendry P., (2002). Energy production from biomass (part 1): overview of biomass. Bioresource Technology, 83, 37 - 46.
9. Perwich, A. D., Justin, R., Chris, J., Kevin, B., and Scott, M. L. (2012). Direct carbon fuel cell: A proposed hybrid design to improve commercialization potential. Journal of Power Sources 213, 275-286.
10. Klass, D. L. (ed.). (1981). ''Biomass as a Nonfossil Fuel Source, American Chemical Society Symposium Series 144.'' American Chemical Society, Washington, DC.
11. Zhang, H., Xiao, R., Jin, B., Xiao, G., Chen, R. (2013). Biomass catalytic pyrolysis to produce olefins and aromatics with a physically mixed catalyst. Bioresour. Technol., 140, 256–262.
12. Cao, D., Sun, Y., Wang, G. (2007). Direct carbon fuel cell: Fundamentals and recent developments. Journal of Power Sources, 167, 250–257.
13. Radetzki, M. (1997). The economics of biomass in industrialized countries: an overview. Energy Policy. Vol. 25, No. 6, pp. 545-554. PII:S0301-4215(97)00043 -8.