3rd International Engineering Conference (IEC 2019)
Federal University of Technology, Minna, Nigeria

Electricity Generation using Locust Bean Waste and Coal in a Molten Carbonate Direct Carbon Fuel Cell

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

ABSTRACT

The quest for a sustainable source of energy has made researchers turn towards direct carbon fuel cell (DCFC). It is a device that directly converts the chemical energy of a biomass or fossil fuel into electrical energy. The combination of the coal and a renewable biomass Locust bean waste (LBW)(Parkia Biglobosa) can enhance the electrochemical performance of the DCFC. Pyrolysis pre-treatment process was initially carried out at heating rate of 10°C/min. This was done for each of the sample and their combination. The pyrolyzed biomass for both of them was then used to determine the electrochemical performance of DCFC using molten carbonate salt as electrolyte and using five different resistor loads (1Ω, 2Ω, 3Ω, 4Ω & 5Ω). Performance of coal in the DCFC was observed to be better than Parkia Biglobosa. However upon combination of both solid fuels, an enhanced performance was observed. At a temperature of 800°C and resistance of 1Ω, the combined fuel showed an open circuit voltage of 1.16 V, current density of 43.2 mA/cm^2, power density of 2.91 mW/cm^2 with 73% efficiency. The SEM result of the carbon fuels was obtained using Nova NanoSEM 200 FEI, Netherlands. The SEM results of the combined fuel were observed to be better. The phase composition of each fuel was determined using Siemens D500 XRD System. The highest peak for the LBW, Coal and the combined fuel was at an angle of 25.988°, 26.24°, 26.637° respectively and the corresponding inter-planar spacing of 3.42Å for LBW fuel and 3.34Å for coal and the other fuel.

Keywords: *Biomass, carbon fuel, direct fuel cell, locust bean waste, coal, Pyrolysis.*

1 INTRODUCTION

Energy is very important to perform the day to day activities of mankind and different alternative energy sources have been the research focus globally. The alternatives from non-renewable forms of energy have been the subject of scientific researches with the aim of addressing the emission challenges of harmful gases released to the atmosphere thus reducing the greenhouse gas effect of climate change and global warming. For developing country like Nigeria, the electrical energy supply is grossly inadequate for the growing population. Thus there is a need to look inward for more sustainable and renewable energy sources from biomass and its blend with other energy sources. Most developing economics will adopt renewable energy, since fossil fuels are limited in supply and will eventually run out of supply. The combination of biomass and fossil fuel (like coal) will be a good blend for sustainable electrical energy generation. These when properly developed will alleviate the effects of climate change and global warming using the direct carbon fuel cell (DCFC) technology (Dudek *et.al.*, 2018; Adeniyi *et.al.*, 2014; Adeniyi & Ewan, 2012; Jain *et.al.*, 2009,2007).

A sustainable modern industrial economy can only be achieved through electrical power generation. The direct carbon fuel cell (DCFC) technology offer a viable technique that can practically produce electricity that is safe, relatively simple, cost effective, remarkably efficient, reliable, environment friendly and a more effective way to improve conventional power generation. Coal is a fossil fuel which is abundant in nature and is reponsible for more than 30% of the world primary energy generation. It has been estimated that this forecast will slighty increase or remain steady until 2030 showing that coal will still be relevant for the future. The conventional method of power generation from coal has contributed to global warming and climate change and thus the DCFC technology offer an efficient and enviroenmenatlly benign way of utilizating the energy stored in coal (Kacprzak *et.al.*, 2019; Cooper & Berner, 2005; Munnings *et.al.* 2014; Arenillas *et.al.*, 2013; Li *et.al.*, 2010).

A direct carbon fuel cell is an electrochemical device that efficiently converts the chemical energy of a carbon rich fuel directly to electrical energy without burning the fuel. The DCFC gives off a pure stream of carbon dioxide that can be captured without incurring additional costs of collection and can be used in other industrial requirements such as in the oil and gas industry. In the DCFC technology, solid carbonaceous fuels are used and directly oxidized at the anode surface. Different carbon fuels, such as coal, biomass, or blends of these are exposed to high temperature conversion, the fuel is electro-oxidized to CO_2 at anode compartment creating electricity. A conversion efficiency rate of 80% is achievable depending on the type of carbon fuel applied; it could reduce carbon emissions by 50% and off-gas volume by 10 times when compared to conventional coal- fired power stations of about 35% efficiency. This increased efficiency results in a beneficial pay off for DCFC development. Fuel produced from waste offers many benefits (Giddey *et.al.*, 2012; Jia *et.al.*, 2010; Declaux *et.al.*, 2010; Cooper & Cherepy, 2008; Cao *et.al.*, 2007; Dicks, 2006; Cherepy *et.al.*, 2005; Zecevic *et.al.*, 2004; Larminie & Dicks, 2003; Hoogers, 2003).

The direct carbon fuel cell offers a higher efficiency and lower emissions in the production of electricity; it is portable and easy to construct. The direct carbon fuel cell use of biomass materials as its fuel source makes it economically viable for waste management and reduction of greenhouse effect. Nigeria as a country is challenged with the lack of adequate electricity to power its economy, which is a major factor affecting the development of most third world countries like: Nigeria, Burkina Faso, Burundi, Niger, Tanzania and others. This paper investigate the use of biomass (locust bean waste (LBW)), coal and the blend to generate electricity using the DCFC technology.

2 METHODOLOGY

Two types of samples were selected for investigation; Locust bean waste (LBW) and Bituminous coal (Figures 1 and 2). Locust bean waste was obtained from Niger State and carefully sorted, sun dried and then reduced in size. This sample was subjected to pyrolysis at 500°C at Badeggi Research Centre Bida, Niger State and the char obtained was ground to fine particles. The same process was carried out for the coal sample obtained from Kogi state and the combination of the two sample simultaneously. A portion of the char was appropriated for proximate and ultimate analysis (Ash content, Volatile matter, Fixed carbon, Moisture content). The proximate analysis was carried out using an ELTRA CHS-580 Analyser (Netherlands). The phase compositions of the carbon samples thus obtained were evaluated using X-ray diffraction analysis (XRD, Netherland) and the Scanning Electron Microscopy (Nova NanoSEM 200 FEI, Netherlands). An EDS system (EDAX, Netherlands) was also used to characterise the morphology and chemical composition of carbon particles used as solid fuel.

The fuel cell experimental set-up was developed for the electrochemical operation of the molten carbonate direct carbon fuel cell (MCDCFC). The electrolyte consisted of sodium carbonate and potassium carbonate, both saturated to a wire mesh to hold it together and subjected to different temperature of 500°C to 800°C. 38 mol% of Na_2CO_3 and 62 mol% of K_2CO_3 were measured, mixed and transferred to a stainless steel plate. The mixture was subjected to high temperature using the blacksmith fire and was stirred continuously to obtain homogeneous mixture.

Figure 1: Locust bean waste (LBW)

Figure 2: Bituminous coal

At a temperature of 1159°C - 1310°C the carbonate salt mixture changed to molten state, the mesh wire was saturated in the molten mixture so that upon cooling, the molten carbonate stuck to the mesh (Adeniyi *et al.*, 2014; Cooper & Berner, 2005). The carbon fuel is mixed with carbonate salts (sodium and potassium carbonate) as 15 wt.% of carbon fuel, 46.6 wt.% of Na_2CO_3 and 53.4 wt.% of K_2CO_3. The sodium carbonate and potassium carbonate were mixed with individual weight of 13.98 g and 16.02 g, and mixed with 45 g of the carbon fuel (Adeniyi and Ewan, 2012; Cooper and Cherepy, 2008).

3 RESULTS AND DISCUSSION

Tables 1 and 2 give the type of analysis that was carried out on the locust bean waste (LBW), coal and their blend after pyrolysis. The proximate and ultimate analysis was conducted at the National Cereal Research Institute, Badeggi in Niger state where the moisture content, volatile matter, fixed carbon and ash content and as well as the carbon (C), nitrogen (N), hydrogen (H), sulphur (S), oxygen (O) content and the calorific values were obtained.

Table 1: Proximate analysis of LBW, coal and blend

Sample	Moisture Content	Ash Content	Volatile Matter	Fixed Carbon
LBW	3.0	8.0	67.0	22.0
Coal	2.4	6.9	68.8	21.9
LBW and Coal	1.82	8.0	64.18	26.0

Table 2: Ultimate analysis of LBW, coal and blend

Sample	C wt.%	H wt.%	O wt.%	N wt.%	S wt.%	Calorific Value MJ/Kg
LBW	3.92	4.8	36.4	0.4	0.2	21.6
Coal	6.43	8.2	27.24	0.08	0.18	21.9
LBW and Coal	5.84	6.8	33.8	0.8	0.2	21.4

3.1 LBW CARBON FUEL

The carbon fuel in the molten carbonate direct carbon fuel cell (MCDCFC) performance at temperatures of 500°C, 600°C, 700°C and 800°C are shown in Figures 3 and 4. These include the SEM and XRD pattern for the locust bean waste fuel pyrolyzed at 500°C. Figure 3 shows the XRD of locust bean waste carbon sample used in the DCFC. The highest peak is at an angle of 25.988°(2θ-axis), with corresponding d-spacing of 3.42Å and a relative intensity of 100%. The peak value suggests a disordered form of carbon and this is a favourable criteria for application in the direct carbon fuel cell (Dudek *et al.*, 2018; Adeniyi *et al.*, 2014; Cooper & Berner, 2005). Figure 4 shows the SEM micrograph for the biochar from the LBW. This shows the size distribution and structure of the pyrolyzed carbon sample. This contains a combination of large particles with smaller ones which shows the interaction of the carbon particles.

Figure 5 presents the MCDCFC performance of the carbon sample used in the direct carbon fuel cell. The voltage increased with increase in the temperature, reaches a maximum, and finally falls at higher current densities.

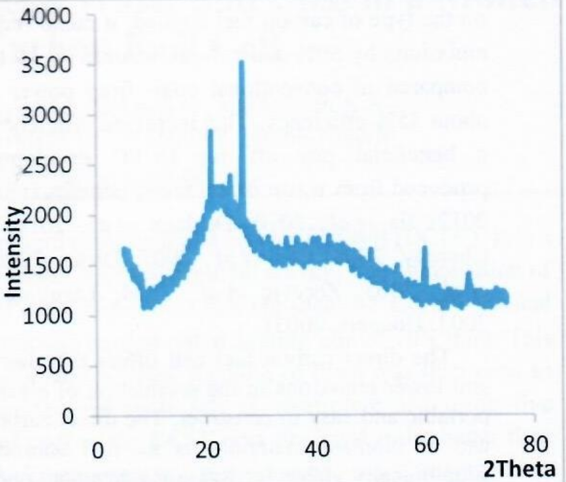

Figure 3: XRD pattern for pyrolyzed LBW at 500°C

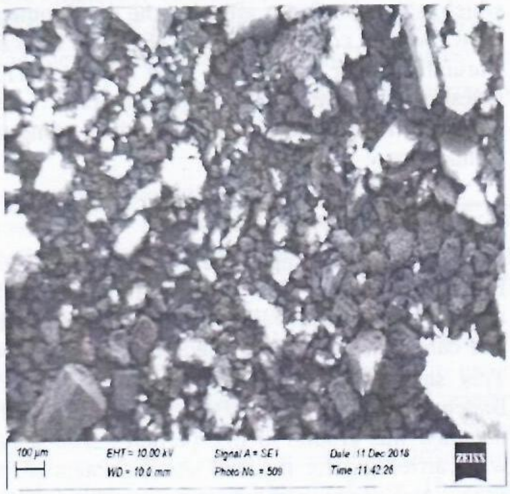

Figure 4: SEM of locust bean waste fuel

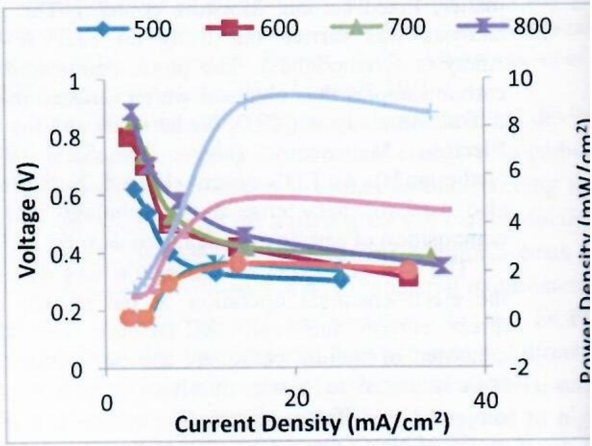

Figure 5: DCFC performance for Locust bean waste fuel

The current density and power density have high values at 800°C. At this temperature, the carbon fuel is consumed at the anode side of the fuel cell and a porous surface created on the electrolyte leading to a sharp rise in the current density. It was also observed from Figure 4 that the carbon particle have finer grain size and more homogeneous microstructure, and the surface morphology enhances the current density (Munnings *et al*., 2014; Jia *et al*., 2010; Jain *et al*., 2009).

3.2 COAL CARBON FUEL

There was a slight difference in the DCFC performance of carbon fuel from coal as compared with that in Figures 3 to 5 at temperature 500-800°C. Figures 6 to 8 shows that the carbon fuel from coal gave a better performance than what was obtained from LBW carbon fuel. Figure 6 displays the X-ray diffraction pattern of the coal carbon fuel pyrolyzed at 500°C. The result obtained showed the degree of disordered graphite content and the sharp peaks indicates the presence of silica, oxygen and other impurities identified by the STOE Databank spectra. It was also observed that the presence of non-crystallites increases the surface area and thus produced improved current density. The peak at 26.24° corresponds to quartz (crystalline SiO2). The inter-planar spacing of the carbon particle is 3.34Å, which indicates the presence of larger reactive sites units. These are indications of the suitability of the coal carbon fuel in the application of DCFC (Arenillas *et al*., 2018; Kacprzak *et al*., 2017).

Figure 7 represents the SEM micrograph of the coal carbon fuel sample. The fuel showed larger particle sizes, irregular shapes and fine grain sized particles. It was observed that the higher the current density the finer the surface morphology of the sample. However it could be deduced that the carbon fuel from coal is a better fuel when used in the direct carbon fuel cell because it possess higher calorific value. From Figure 8, it was noticed that the voltage increased with corresponding increase in the temperature, up to a point where there was a slight drop in the voltage reading. The coal carbon fuels also display higher current density at higher temperature (Li *et al*., 2010; Jain *et al*., 2009).

3.3 COMBINED CARBON FUEL

Figures 9 to 11 represents the electrochemical performance of the combined carbon fuels used in the fuel cell. The X-ray diffraction pattern for the combined carbon particle is represented in Figure 9. The presence of non-crystallites increases the surface area and thus producing improved current density.

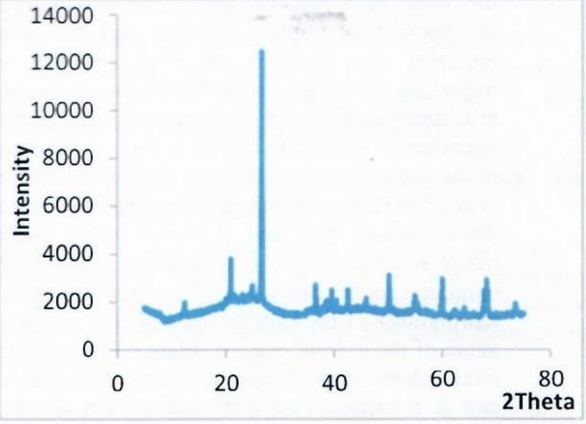

Figure 6: XRD pattern for coal pyrolyzed at 500°C

Figure 7: SEM pattern for coal carbon fuel

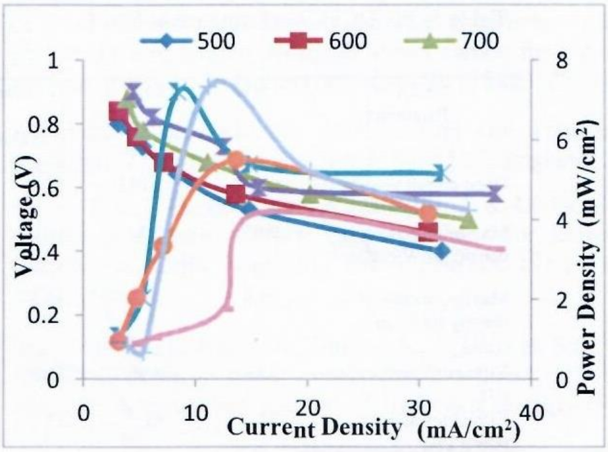

Figure 8: DCFC performance for coal fuel

The highest peak is at an angle 26.637° with corresponding d-spacing of 3.34Å on a relative intensity of 100%, which is the same with what was obtained for the coal carbon fuel. The result obtained shows the degree of disordered graphite content and the sharp peaks indicates the presence of silica, oxygen and other impurities identified by the STOE Databank spectra. The disordered carbon particle is an important property in the operation of DCFC. Pyrolysis is vital to the disorderliness of the carbon particles (Cooper & Cherepy, 2008; Zecevic *et al.*, 2004). Figure 10 represents the SEM micrograph of the combined fuel and it shows larger particle sizes, irregular shapes and fine grain particles with slightly homogenous microstructure. The finer the particle surface morphology of the sample the higher it influences on the value of the current density. Figure 11 reveals the overall electrochemical performance of the combined carbon fuel and it interprets that a higher current density of 43.2 mA/cm^2 was obtained at 800°C alongside the power density. 8.10 mW/cm^2 was also obtained as the peak power density value. The performance of the DCFC is enhanced when coal is blended with LBW, which could lead to a lower CO_2 emission from the operation. This itself will have significant effect on the reduction of climate change and global warming when compared to the conventional burning of coal.

Figures 5, 8 and 11 shows the characteristics of power, current and voltage curves for a molten carbonate direct carbon fuel cell (MCDCFC). Some electrochemical parameters are presented in Table 3. The combined fuel (LBW and Coal) has the highest power efficiency of 73% at 800°C while LBW (locust bean waste) had the lowest at 54°C at same operating temperature. The open circuit voltage, peak power density, current density at 73% voltage efficiency proved to be the best result amidst the carbon fuel samples.

Table 3: MCDCFC performance at 800°C

MCDCFC Parameter	LBW	Coal	Combined Fuel (LBW & Coal)
Open circuit voltage (V)	0.90	1.012	1.16
Maximum power density (mW/cm^2)	9.05	7.32	8.10
Maximum current density (mA/cm^2)	35.6	36.8	43.2
Voltage at peak power (V)	0.89	0.90	1.08
Efficiency at peak power (%)	54	61	73

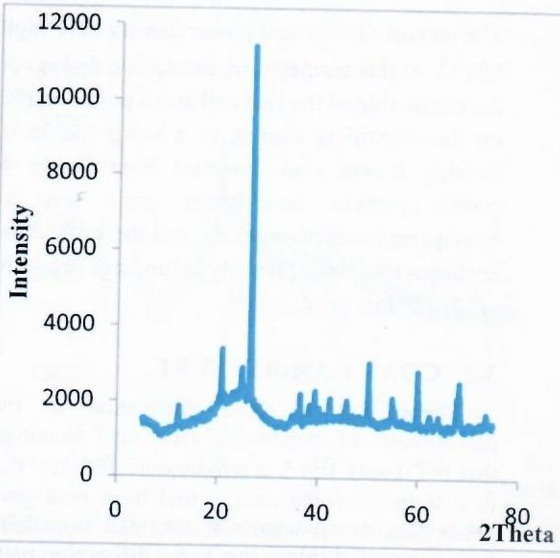

Figure 9: XRD for combined fuel (LBW and Coal)

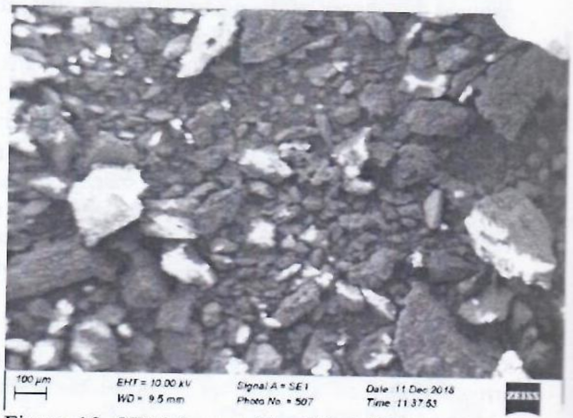

Figure 10: SEM for combined fuel (LBW and Coal)

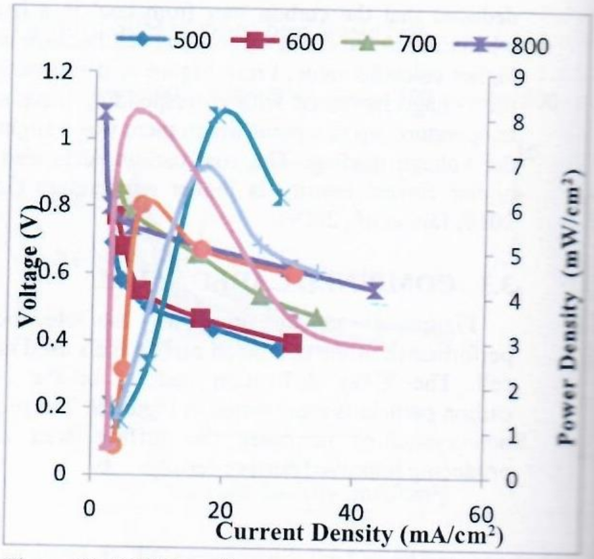

Figure 11: DCFC performance for combined fuel.

4 CONCLUSION

The investigation of the molten carbonate direct fuel cell showing the electrochemical performance of locust bean waste, coal and the combined fuel were carried out. The performance for the combined fuel was higher than that obtained from coal and locust bean waste. The open circuit voltage of the combined fuel is 1.16 V and is higher than 0.90 V of locust bean waste and 1.012 V for coal. The optimum peak power density recorded for the combined fuel (LBW & Coal) is 8.10 mW/cm^2, maximum current density of 43.2 mA/cm^2 with a resistance of 1 Ω. An efficiency of 73% was obtained from the combined carbon fuel which gave it a better performance in the direct carbon fuel cell operations. The scanning electron micrograph and X- ray diffraction reveals that the combined carbon fuels contain large sized particles with the highest peak of 26.637° with corresponding d-spacing of 3.42 Å similar to the coal carbon fuel. It was observed that finer particle morphology led to high current density and the presence of non-crystallites improved the current and power densities achievable with the fuel cell.

REFERENCES

Adeniyi, O.D. & Ewan, B.C.R. (2012). Electrochemical conversion of switchgrass and poplar in molten carbonate direct carbon fuel cell. *International Journal of Ambient Energy*, 33:4, 204-208.

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, *Journal of Energy Challenges & Mechanics,* 1(4) 6, 1-6.

Arenillas, A., Menéndez, J.A., Marnellos, G.E., Konsolakis, M., Kyriakou, V., Kammer, K., Jiang, C., Chien, A. & Irvine, J.T.S. (2013). Direct coal fuel cells (DCFC).The ultimate approach for a sustainable coal energy generation. *Bol. Grupo Español Carbón*, 29, 8-11.

Cao, D., Sun, Y., Wang, G. (2007). Direct carbon fuel cell: Fundamentals and recent developments. *Journal of Power Sources*, 167(2), 250-257.

Cherepy, N.J., Krueger, R., Fiet, K.J., Jankowski, A.F. & Cooper, J.F. (2005). Direct conversion of carbon fuels in a molten carbonate fuel cell. *Journal of the Electrochemical Society*, 152(1) A80-A87.

Cooper, J.F., & Berner, K. (2005). The carbon/air fuel cell, conversion of coal-derived carbons" in: *The Carbon fuel Cell Seminar*, Palm Spring, CA, Nov. 14th, UCRL-PRES-216953, 1-16.

Cooper, J.F., & Cherepy, N. (2008). Carbon fuel particles used in direct carbon conversion fuel cells. *US Patent Publication,* No. US 2008/0274382 A1.

Desclaux, P., Nürnberger, S., & Stimming, U. (2010). Direct carbon fuel cells", in R. Steinberger-Wilckens, W. Lehnert (eds.) *Innovations in Fuel Cell Technologies*, RSC Energy and Environment Series No. 2, Royal Society of Chemistry, Cambridge, 190-210.

Dicks, A.L. (2006). The role of carbon in fuel cells. *Journal of Power Sources*, 156, 128-141.

Dudek, M., Adamczyk, B., Sitarz, M., Sliwa, M., Lach, R., Skrzykiewicz, M., Raźniak, A., Ziąbka, M., Zuwala, J. & Grzywacz (2018). The usefulness of walnut shells as waste biomass fuels in direct carbon solid oxide fuel cells, *Biomass and Bioenergy*, 119, 144–154.

Giddey, S., Badawal, S.P.S., Kulkarni, A. & Munnings, C. (2012). A Comprehensive Review of Direct Carbon Fuel Cell Technology. *Progress in Energy and Combustion Science*, 38, 360 – 399.

Hoogers, G. (2003). Fuel Cell Technology Handbook. *CRC Press LLC*, Florida.

Jain, S.L., Lakeman, J.B., Pointon, K.D. & Irvine, J.T.S. (2007). A novel direct carbon fuel cell concept. *Fuel Cell Science & Technology.* 4, 280-282.

Jain, S.L., Lakeman, J.B., Pointon, K.D., Marshall, R. & Irvine, J.T.S. (2009). Electrochemical performance of a hybrid direct carbon fuel cell powered by pyrolysed MDF. *Energy Environ. Sci.* 2,687-693.

Jia, L., Tian, Y., Liu, Q., Xia, C., Yu, J., Wang, Z., Zhao, Y., & Li, Y., (2010). A direct carbon fuel cell with (molten carbonate)/(doped ceria) composite electrolyte. *J. Power Sources*, 195:5581-5586.

Kacprzak, A., Kobyłecki, R. & Bis, Z. (2017). The effect of coal thermal pretreatment on the electrochemical performance of molten hydroxide direct carbon fuel cell. *Journal of Power Technologies* 97 (5) (2017) 382–387.

Larminie, J. & Dicks, A. (2003). Fuel cell systems explained. 2nd edition, John Wiley & Sons Ltd., England.

Li, X., Zhu, Z.H., de Marco, R., Bradley, J. & Dicks, A. (2010). Evaluation of Raw Coals as Fuels for Direct Carbon Fuel Cells. *Journal of Power Sources*, 195 (13): 4051 – 4058.

Munnings, C., Kulkarni, A., Giddey, S., & Badwal, S.P.S. (2014). Biomass to power conversion in a direct carbon fuel cell. *International Journal of Hydrogen Energy*, 39, 12377-12385.

Zecevic, S., Patton, E.M., & Parhami, P. (2004). Carbon-air fuel cell without a reforming process. *Carbon*, 42, 1983-1993.