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Utilization of Organic Waste in a Direct Carbon Fuel Cell for Sustainable Electricity Generation

Andrzej Kacprzak * and Renata Włodarczyk

Department of Advanced Energy Technologies, Faculty of Infrastructure and Environment, Czestochowa University of Technology, Dąbrowskiego 73, 42-201 Czestochowa, Poland; renata.wlodarczyk@pcz.pl
* Correspondence: andrzej.kacprzak@pcz.pl

Abstract: There is much organic waste that comes from by-products of agriculture and product processing, solid waste from livestock, and municipal waste. Conventional methods that are widely used for the treatment and management of organic fractions of waste are landfilling, composting, anaerobic digestion, incineration, gasification, and pyrolysis. Among the above methods, pyrolysis is a relatively simple, robust, and scalable technology for transforming diverse organic waste feedstock into renewable energy products. Recently, the electrochemical conversion of biochar into electricity in direct carbon fuel cells (DCFC) has also been investigated and shown to be feasible and highly efficient. This paper focuses on the utilization of organic waste as a fuel and the investigation of their characteristics during electrochemical reactions in molten hydroxide direct carbon fuel cells (MH-DCFCs). Organic waste of different origins (the food-processing industry, urban and suburban areas, municipal solid organic waste, sewage sludge) with diversified characteristics was used as the main feedstock. The lowest power density was determined for sewage sludge (5.1 mW cm^{-2}), and the best results were obtained for peanut shells (53.14 mW cm^{-2}). This study concludes that higher elemental carbon, lower ash content and the presence of reactive surface oxygen functional groups in biochar obtained from organic waste might contribute to better cell performance. Moreover, the research establishes the potential of carbonized organic waste as a prospective alternative fuel source for power generation in an MH-DCFC.

Keywords: direct carbon fuel cell; molten hydroxide electrolyte; biochar; organic waste; waste utilization; waste to energy

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1. Introduction

Environmental problems involving air, soil, and water pollution, together with the growth of both energy demand and the consumption of non-renewable resources, will become inevitable in the coming decades. Another important challenge is the rising production of different types of waste in households and industrial plants. Global quantities of waste are continually increasing with the growth in the world population, increasing urbanization, economic development, and excessive consumerism [1]. The treatment and disposal of solid waste is one of the most important problems and greatest challenges facing mankind.

It is estimated that, globally, more than 2 billion tons of municipal solid waste were generated in 2016. This number is expected to grow to 2.59 billion tons by 2030, and waste generation across the world is expected to reach 3.40 billion tons by 2050 [2].

Organic waste comprises the majority of solid waste composition. The data presented in Figure 1 compare solid waste composition between 2012 values and values projected for 2025 for low- and high-income countries. As can be seen, low-income countries have an organic fraction of 64% compared to 28% in high-income countries [3]. Organic waste can come from the following dominant sources: households (organic fraction of municipal solid waste, e.g., domestic organic waste, restaurant and kitchen waste, office

buildings, institutions and small businesses, organic garbage, etc.), agriculture, and the food-processing industry (agricultural crop residues and organic byproducts of food production, e.g., stalks, leaves, seed pods, husks, and roots), urban and suburban areas (grass, fallen leaves, branches from shrubs, and tree pruning) or municipal wastewater treatment plants (sewage sludge).

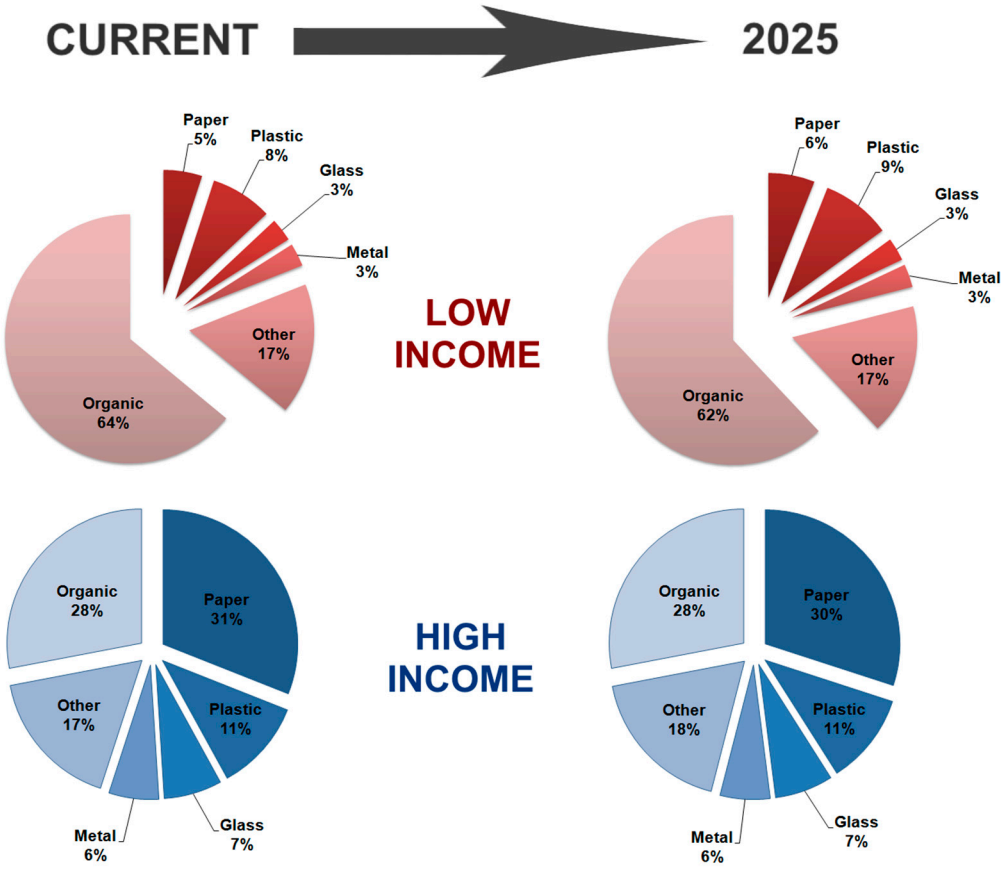


Figure 1. Solid waste composition by income and year. The figure was redrawn based on [3].

Conventional methods that are widely used for the treatment and management of organic fractions of waste are landfilling, composting, anaerobic digestion, incineration, gasification, and pyrolysis [3].

Landfilling is found to be an economical way of disposing of different types of waste compared to other waste-management techniques. However, waste disposal through landfill causes many serious environmental problems, such as the release of methane into the atmosphere, which is the second most plentiful anthropogenic greenhouse gas, considerable amounts of unpleasant odour, pathogenic microorganisms, and the generation of leachate, which can potentially infiltrate the environment (especially into soil and the groundwater) [4]. Moreover, according to European Council directive 1999/31/EC [5], the deposition of waste in landfills should, as far as possible, be minimized to reduce the environmental impact.

The process whereby microorganisms break down organic matter into simpler substances, water, CO_2, and heat is known as composting. Composting produces a high-quality and valuable final product that helps to return nutrients to the soil and reduces the amount of waste being sent to landfill. This, therefore, is a sustainable method of organic waste management, but requires a relatively large area, odour control, and the provision of suitable conditions for the process.

Anaerobic digestion (AD) is a naturally occurring process that involves the breakdown of organic compounds by microorganisms in a non-oxygen atmosphere to produce mainly biogas (solid and liquid residues are also formed). AD typically takes place within an

enclosed vessel known as a bioreactor. This type of treatment is a highly effective and safe way of dealing with organic waste. Produced biogas can be used as a source of energy for heat or power generation and the solid/liquid residues can be spread safely on agricultural land, supplying nutrients. Unfortunately, not all types of organic waste are compatible with anaerobic digestion. Wood and other waste materials containing lignin serve as prime examples of organic waste that is not suitable for AD. Typically, these materials are disposed of using other alternative technologies, such as composting or incineration/gasification combined with energy recovery. Moreover, microorganisms used for AD process are very sensitive to changes in environmental conditions inside the bioreactor. Mayor factors affecting microbial activity are temperature, pH, moisture, oxygen concentration, presence of toxic elements and compounds [6].

Conventional incineration, pyrolysis, and gasification technologies are thermal conversion methods currently used to generate electricity and heat from organic waste [7]. Incineration, pyrolysis, and gasification are a practice which generates heat (and/or steam), biochar/liquid hydrocarbons/gas and syngas from waste, respectively, as well as electricity. However, they need complex units to handle organic waste as a very low-grade fuel and also costly equipment for cleaning the flue gas and syngas, so they are only economic at large scales [8].

However, the huge volumes that are produced globally alongside the diversity that these waste present makes them ideal candidates to be used for high-value applications with the potential to provide a significant amount of energy. The energy sector is considered to be a perfect match, because of its need to continuously meet a growing energy demand. Energy conversion from different waste can be obtained by utilising different technologies as shown in Figure 2. Each one of these Waste-to-Energy (WtE) solutions has specific characteristics, and can be more or less feasible depending on many parameters [7]. Waste is now not only an undesired product of society, but a valuable energy resource as well. Selected organic waste can either be reduced or transformed into beneficial products through the application of new and innovative approaches and technologies for the reuse of these resources as substrates for energy generation.

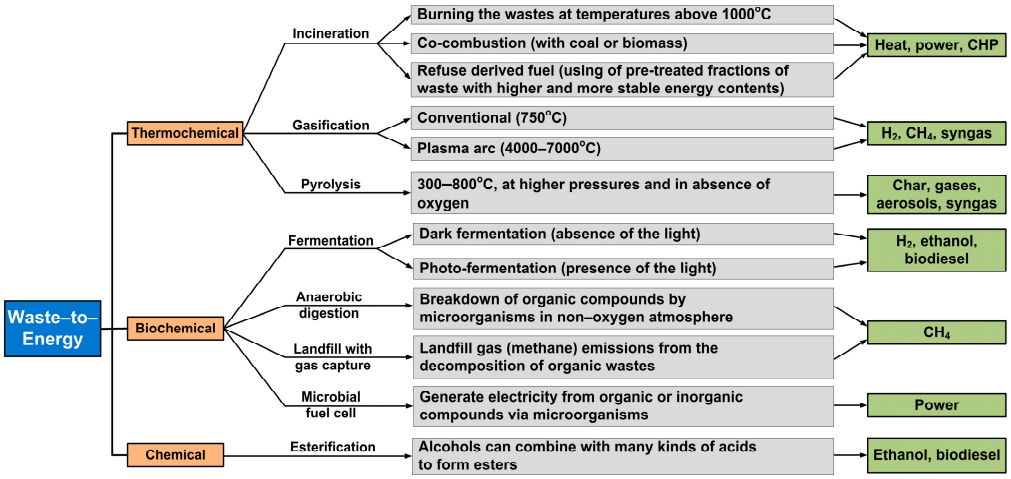


Figure 2. Waste-to-energy processes and technologies. The figure was reproduced based on reference [7].

The utilization of organic fraction of waste can be combined with the generation of energy through its conversion to gaseous fuels (biogas, syngas), which can be used directly in high-temperature fuel cells like a solid-oxide fuel cells (SOFC) or molten carbonate fuel cells (MCFC) after an in-depth cleaning step for the removal of contaminants (especially sulphur and chlorine compounds) below ppm levels [9]. Fuel cell stack coupled with biomass gasifier is one of the most promising energy generation systems for the future, because it is renewable, environmentally friendly and carbon neutral. Moreover, that technology can be applied to medium- and large-scale stationary systems for distributed

power generation. On the other hand, the inclusion of additional system components such as the gasifier and gas cleaning equipment diminishes the overall system efficiency. Therefore, common fuel cell systems with integrated biomass or organic waste gasification are unlikely to achieve electrical efficiencies exceeding 40% [10,11].

One technology that can offer clear advantages over the abovementioned conventional SOFC and MCFC systems including higher waste conversion efficiency (no need to use of gasifiers and gas cleaning systems), low emissions and production of a pure CO_2, which can be easily captured for storage or industrial usage, is direct carbon fuel cells (DCFC). The basic structure of a DCFC is identical to any of the other fuel cells. However, it uses solid carbonaceous fuels (e.g., bituminous and sub-bituminous coals, lignite, biochar, active carbons, carbon black, graphite, coke, etc.) directly at the anode surface in place of a gaseous fuels (e.g., H_2, CH_4 or CO).

As already mentioned, biomass can be converted into useful forms of energy using a number of different processes such as thermo-chemical (combustion, pyrolysis, gasification) and bio-chemical/biological (digestion and fermentation). Among the above methods, the pyrolysis is relatively simple, robust, and scalable technology for transforming diverse biomass feedstocks into renewable energy products: heat, biochar, syngas, and/or bio-oil. What distinguishes pyrolysis from alternative ways of converting biomass to energy is that pyrolysis produces a carbon-rich, fine-grained, porous substance called biochar. Biochar obtained from biomass pyrolysis is frequently regarded as a waste product and is consequently combusted to generate the required heat for the pyrolysis process. Nevertheless, recent research [12,13] indicates that biochar resulting from pyrolysis can serve as a precursor for catalysts, soil amendment to enhance soil quality and promote carbon sequestration, sorbent for removing contaminants from gases, soils, and water, a storage medium for CO_2 and H_2, a material for electrodes in microbial fuel cells to facilitate simultaneous wastewater treatment and power production, and various other applications [14–30]. Biochar can also be burned to produce electricity and heat. However, the efficiency of energy utilization of biochar is low in the case when direct combustion and thermal transformation processes are applied. Recently, the electrochemical conversion of biochar into electricity in direct carbon fuel cells (DCFC) has also been investigated and shown to be feasible and highly efficient [17,28,31]. That technology is currently considered a highly attractive way, especially when environmental concerns are of importance during energy production.

DCFCs can utilize different solid carbonaceous fuels, e.g., fossil coals [14–16] or carbonized biomass of various origins [17–19], even organic waste like coffee grounds [20], corn cob [21], almond shells [22], palm oil waste [23], raw waste wood [24] or wastepaper and bamboo fibre [25]. Refuse fuels such as refuse-derived fuel (RDF), refuse plastic/paper fuel (RPF), which are pellets made from urban waste, and plastics (i.e., polyethylene terephthalate; PET) have also been tested in DCFC systems [26,27].

Hansaem et al. [20] have shown the potential for generating electricity directly from waste coffee grounds (WCG) using a high-temperature DCFC technology. At a cell operating temperature of 900 °C, the WCG-powered DCFC exhibited a maximum power density nearly double that of carbon black (87.2 mW cm^{-2} compared to 46.3 mW cm^{-2}).

Electrochemical performance of a hybrid DCFC (H-DCFC), which utilizes both primary (solid oxide membrane) and secondary (molten carbonate) electrolytes, operated at 750 °C and supplied by biochar derived from corn cob has been examined by Yu et al. [21]. A peak power density of 185 mW cm^{-2} was obtained, which was much higher than the results obtained with the other types of carbon fuel in similar conditions.

Raw and charred walnut shells as solid waste biomass fuels were investigated by Dudek et al. [28]. DCFC based on the solid oxide electrolyte (DC-SOFC) operating within the temperature of 850 °C and supplied by walnut shells carbonized at 450 °C generated a power output of approximately 119 mW cm^{-2} in the presence of CO_2 in the anode chamber.

In another study, Li et al. [29] examined a high-temperature DC-SOFC fuelled by corn straw carbon, which was obtained via a thermal pyrolysis process. The value of the achieved maximum power density was 218.5 mW cm^{-2} at 850 °C.

Adeniyi [30] examined a DC-SOFC fuelled by wheat straws and spruce wood chips. At an operating temperature of 800 °C, the peak power densities recorded for wheat straws and spruce were 66.92 mW cm^{-2} and 57.40 mW cm^{-2}, respectively.

This paper focuses on the utilization of organic waste as a fuel and the investigation of their characteristics during electrochemical reactions in the medium-temperature molten hydroxide direct carbon fuel cell (MH-DCFC). The main novelty of this work is the use an organic waste from various origins (food processing industry, urban and sub-urban areas and especially from municipal solid organic waste and sewage sludge) with diversified characteristics as the main feedstock to produce a biochar via pyrolysis process, which is then used as fuel for high-efficiency MH-DCFC. The scientific novelty of this work is also experimental, establishing the effect of carbonized (pyrolysed) waste sample properties on electrochemical activity in MH-DCFC through correlation with maximum current and power densities.

2. Materials and Methods

2.1. Samples Preparation

Organic materials came from the food processing industry (peanuts shells and sunflower husks), urban and sub-urban areas (grass + leaves and woodchips obtained from trees pruning), municipal solid waste (MSW) generated in the households and sewage sludge taken from a local municipal wastewater treatment plant were chosen for investigation. Synthetic municipal solid waste (sMSW) simulating typical composition of municipal MSW generated in the households were composed by using 6 different organic waste materials, namely, potato and apple peelings, pumpkin and banana peels, egg shells and dog food used to simulate meat waste. According to the ingredients table offered by the manufacturer, dog food was composed of 53.5% carbohydrates, 23% proteins, 13% oils and fats, 2.5% fibres, and 8% ash on a dry basis. It is worth mentioning that the composition of organic fractions of MSW varies from region to region and it depends upon the lifestyle and demographic features.

The utilization of untreated raw organic waste in an MH-DCFC poses challenges due to the significant amount of volatile matter (VM) within the structure of organic material. Those VM can potentially disrupt the electrochemical reactions in the anode compartment and result in performance degradation. Therefore, a thermal pretreatment was employed on all waste materials to produce biochar, enhancing their suitability for use in the fuel cell. The biochar was prepared using a raw organic waste carbonization process, by heating the samples from 300 to 973 K at a rate of 10 K min^{-1} under N_2 atmosphere. Selected waste were placed in a stainless-steel tube reactor (see Figure 3) with an internal diameter of 30 mm and length of 120 mm. Both ends of tube were then closed by ceramic corks and the reactor assembly was placed in a muffle chamber of an electric heating laboratory furnace. Figure 4 shows the heating profile (temperature–time profile) of the pyrolysis (carbonization) of individual samples, which allowed the sample to be heated in a controlled and reproducible manner. After the desired heating time, the reactor was withdrawn from the furnace and cooled down to ambient temperature still under N_2 atmosphere, therefore the obtained biochar samples did not contain moisture that could be absorbed by samples from the air during the cooling process. The resulting biochar was then sieved to a size range of 180–250 µm (in order to compare of the obtained results with research results from other works that have been conducted by authors [17,31–33]) and then stored in a glass desiccator.

After the carbonizing process, biochar obtained from leaves and grass was mixed together in a 1:1 weight ratio. Individual biochar included in the synthetic municipal waste were mixed together in the weight proportions shown in Table 1.

A sample preparation flowchart is shown in Figure 5. It is a flow chart showing the sequence of organic waste treatment to obtain biochar—suitable fuel for the MH-DCFC supplying.

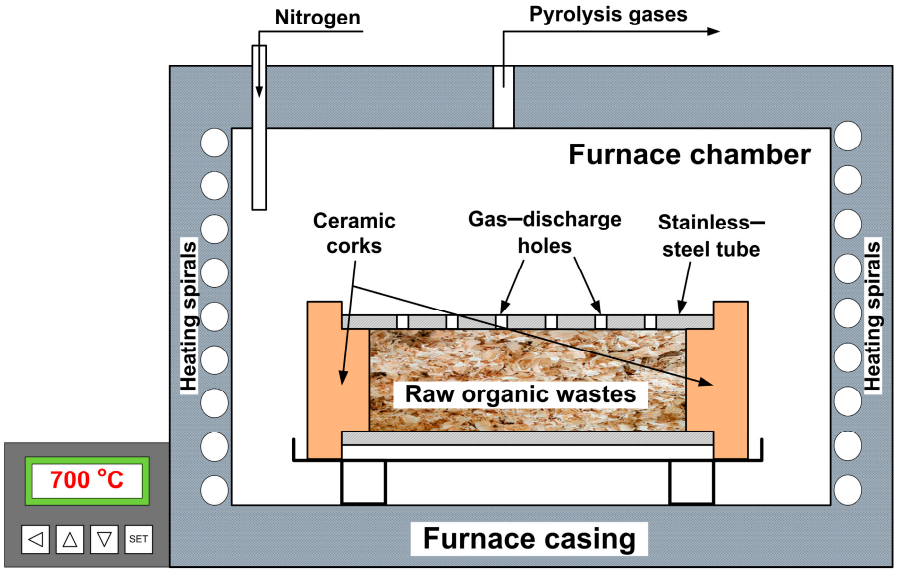


Figure 3. Schematic diagram of the tube reactor for waste carbonization.

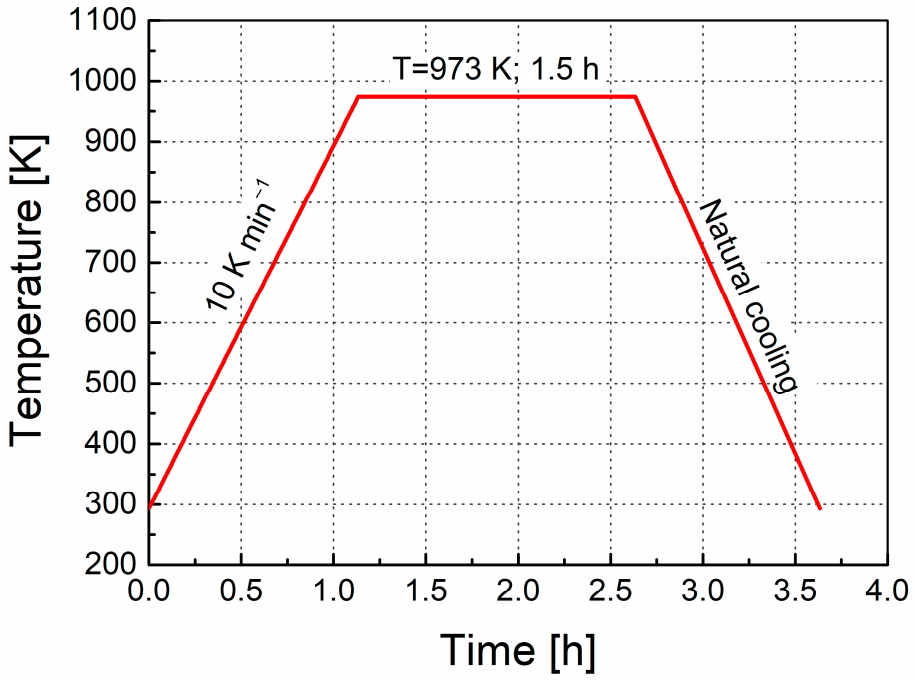


Figure 4. Temperature time profile during the carbonization of organic waste.

Table 1. Proportions of individual organic waste in the synthetic MSW.

Weight Proportions [wt.%] (Dry Material—After Carbonization)					
Potato Peelings	**Apple Peelings**	**Pumpkin Peels**	**Banana Peels**	**Egg Shells**	**Dog Food**
5.8	5.4	6.9	3.8	28.2	49.9

2.2. Samples Preparation

Obtained biochar was provided for proximate, ultimate, spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses.

Proximate analysis was conducted based on the following standards: moisture (M): ISO 589:2006, ash: ISO 1171:2002, volatile matter (VM): ISO 562:2010.

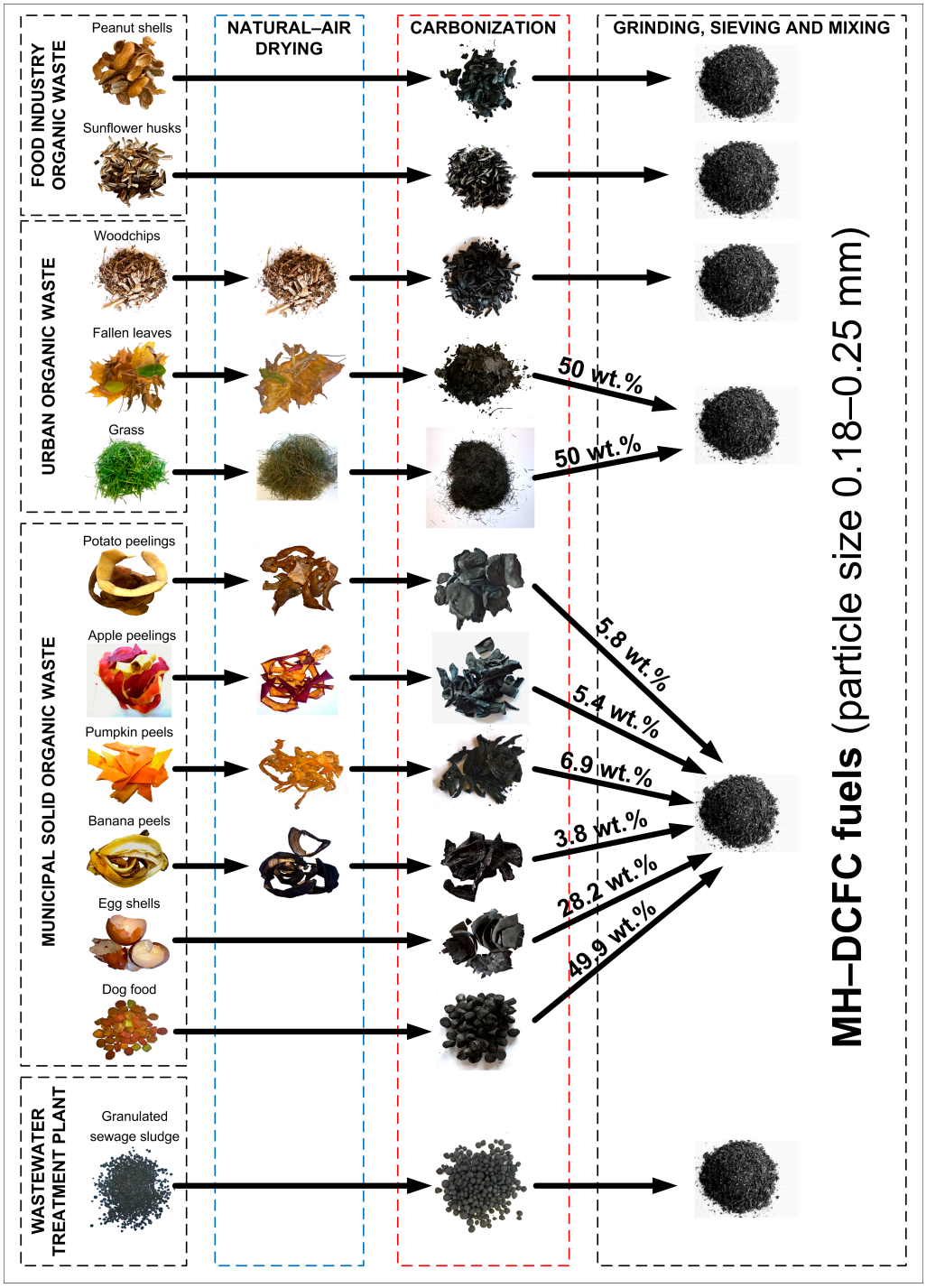


Figure 5. Flowchart of organic waste preparation for MH-DCFC.

The ultimate analysis of the content of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) was carried out in an elemental Leco TruSpec CHNS analyser according to ISO 29541:2010 and ISO 19579:2006 standards. Biochar oxygen concentrations were obtained by difference as follows:

$$O(\%) = 100 - (C^d + H^d + N^d + S^d + Ash^d) \quad (1)$$

To determine the type of surface oxygen-containing functional groups, a Fourier Transform Infrared spectroscopy (FTIR) analysis was performed on a JASCO FT/IR-6200 spectrometer equipped with a liquid nitrogen-cooled MCT (Mercury Cadmium Telluride—

HgCdTeO) detector. To obtain the IR spectra of carbonized samples the KBr pellet forming method was used. About 0.1 mg of dry sample and 200 mg of KBr was finely grounded and mixed together in an agate mortar. After that, the mixture was placed in the pellet-forming die and a force of approximately 9 tons was applied under a vacuum for 7 min to form transparent pellets. The FTIR spectra were recorded in the range of mid-infrared (4000–500 cm^{-1}) collecting 50 scans per sample at a resolution of 4 cm^{-1}. Identification of functional groups in the spectrum was performed with the KnowItAll® database search software package from Sadtler.

Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDX) was applied to analyse the chemical and structural properties of biochar produced from different organic waste. The surface morphology and chemical composition was analysed using Philips XL30/LaB6 scanning electron microscope.

X-ray diffraction (XRD) is a widely used method for analysing the crystalline nature and structure of biochar. Phase analysis of carbonized organic waste was conducted using an X-ray XRD Seifert 3003 T-T diffractometer. The investigations were performed with a cobalt lamp emitting radiation with a wavelength of CoK = 0.17902 nm. The diffractometer operated with the following parameters: power supply: 30 kV, current intensity: 40 mA, measurement step: 2 degrees, and a counting time of 10 s for each impulse.

2.3. MH-DCFC Performance Test

2.3.1. MH-DCFC Construction Details

The MH-DCFC model used in this study was built only from nickel and its alloys. In addition, anodic and cathodic chambers were separated in order to prevent mixing of gases—CO_2 above the anode and excess air above the cathode. The construction details of the MH-DCFC prototype are showed in Figure 6. The main cell container (inside diameter of 83 mm, height of about 147 mm) was manufactured from the Nickel® 201. In that construction of cell, the anode was made from the Nickel® 201 and the cathode was made of Ni-based Inconel® alloy 600. The anode and cathode were specially designed constructions made of pipes with the outside diameters of 19.1 mm and 42 mm, respectively. The current and power densities were calculated for the measured anode surface area of 17 cm^2. The components of the prototype, in particular the anode and cathode materials, were subjected to simultaneous oxidation-lithiation process which is described in details elsewhere [31].

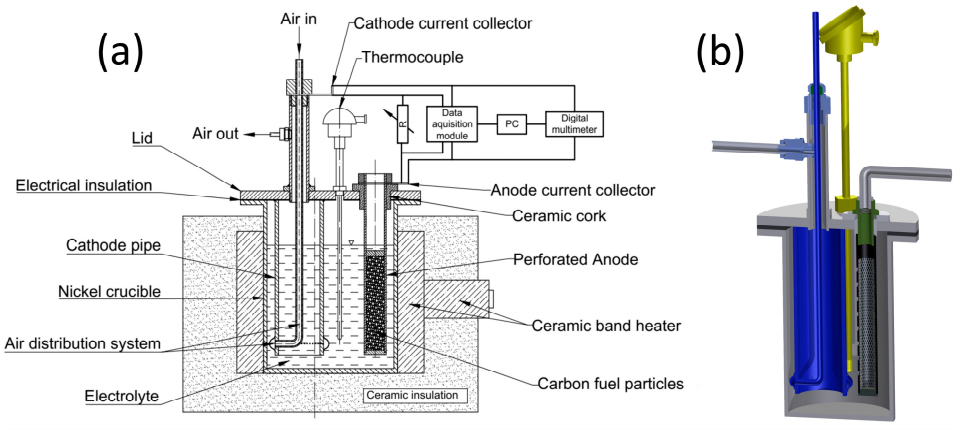


Figure 6. A schematic diagram of the MH-DCFC experimental apparatus: (**a**) design, (**b**) 3D visualization.

The standard cell notation (line notation) for tested MH-DCFC can be written as follows:

Biochar | Li-doped NiO | Ni | NaOH-LiOH | Ni | Li-doped NiO | Air (2)

2.3.2. Test Methodology

The cell performance tests were conducted in the batch-mode with granulated pyrolyzed organic waste (particle size: 0.18–0.25 mm) in the anode compartment. Compressed air (0.15 MPa) was used as the oxidant agent, and supplied into the cathode compartment at a flow rate of 0.5 dm_n^3 min^{-1}.

At the beginning of each test eutectic mixture of NaOH (90 mol%) with LiOH (10 mol%) was prepared and then heated up to a temperature of 723 K. After the desired temperature was reached and the electrolyte was completely molten, both the cathode and the anode were slowly immersed into the electrolyte and the main electric parameters were recorded.

The electrolyte temperature was determined by a K-type thermocouple (NiCr-NiAl) and was maintained at the desired value by an electronic temperature controller. The data acquisition module Advantech USB-4711A was used for the measurement of the cell voltage and the decrease in the voltage on an external resistor. In order to determine the cell current and power at various loads an external resistance setup MDR-93/2-52 was used and connected to the cell circuit, thus providing the possibility to adjust the electrical resistance of the external circuit (in range 0.1–10,000 Ω). The Tektronix DMM 4040 digital multimeter was used to measure the open circuit voltage of the fuel cell. The acquisition module and multimeter were connected to a personal computer (PC) where the data were displayed and stored. The amount of air fed into the cell was controlled by a thermal mass flow controller (Brooks 4850) with a local operator interface (LOI) to view, control and configure the control device.

After each test was finished, the heating was turned off and the cell was 'shutdown'. The setup was then cooled down to room temperature and then all its parts were placed in special plastic container filled with roughly 25 L of deionized water. All the elements were kept there for three hours in order to remove the solidified electrolyte. A mechanical stirrer was used to improve the dissolution of the electrolyte. The water–electrolyte mixture was then removed and 25 L of new deionized water was put into the container. The whole procedure was then repeated. Afterwards, the cell elements were removed from the container, cleaned with a soft sponge, and finally again rinsed with deionized water. All the elements were then dried for 3 h in an electric drier.

More details of operation procedures and measurement methodology of the presented MH-DCFC have been described in details in references [16,31–33].

3. Results and Discussion

3.1. Physicochemical Fuel Samples Characterization

3.1.1. Proximate and Ultimate Analysis

The proximate and ultimate analyses of the carbonized waste samples are presented in Table 2.

Table 2. Proximate analysis of the biochar samples obtained from different biomass (dry basis).

Biochar Sample	Proximate Analysis [wt %]				Ultimate Analysis [wt %]				
	Moisture	Ash	VM	FC	C	H	N	S	O
Peanuts shells	0.0003	13.49	11.50	75.01	81.02	1.38	1.24	0.25	2.62
Sunflower husks	0.0003	9.00	16.10	74.90	84.10	2.50	2.40	0.03	1.97
Grass + leaves	0.0008	29.54	14.90	55.56	52.91	1.16	3.01	0.46	12.92
Woodchips	0.0007	28.89	10.29	60.82	56.46	1.05	0.42	0.00	13.18
Sewage sludge	0.0003	67.41	10.05	22.54	27.58	0.71	2.06	2.221	0.02
sMSW	0.0005	44.01	13.00	42.99	44.00	0.89	2.23	0.01	8.86

As can be seen, due to the storage of biochar in a glass desiccator, the moisture content in the samples was negligibly low (<0.001%).

The ash percentage ranged between 9.00 and 67%. Sewage sludge recorded the highest ash content (67.4%), followed by synthetic municipal solid waste (44.0%). The lowest ash content was recorded in the biochar obtained from sunflower husks (9%). With the consumption of fixed carbon in fuel, the ash will remain and accumulate on the anode surface, which is not desirable, because ash acts as a barrier for the carbon to be in contact with the anode surface, and thus severely blocks the active sites of the anode for oxidation. The high ash content can also negatively affect the cell performance due to reactions between mineral compounds and electrolytes (e.g., limiting electrolyte ionic conductivity). Therefore, it can be concluded that the biochar with high ash content will not be the suitable fuel. However, some of the impurities contained in the ash can affect the reactivity of carbon and improve cell performance, as reported in references [34,35].

Volatile matter (VM) content (present in the biochar after the carbonization process) ranged from 10 to 16% and as can be seen it was comparable in all samples, which could be due to the same parameters of the carbonization process. The highest volatile matter content was noted in sunflower husks (16.1%) and the lowest VM content was recorded in both sewage sludge (10.05%) and woodchips (10.29%).

Fixed carbon (FC) ranged between 22.5 and 75% and it is seen that the ash content correlates with the fixed carbon content—the more ash in the sample, the lower the FC content. The fixed carbon (~75%) content was high in both peanuts shells and sunflower husks and the FC value for sewage sludge was very low (22.5%).

The sewage sludge sample has the highest ash and sulphur (>2.2%) content and the lowest carbon (27.5%) and oxygen (0.02%) content, which could contribute to MH-DCFC performance deterioration. In contrast, peanut shells and sunflower husks have the highest carbon (81–84%) content, moderate oxygen content (2–2.5%) and the lowest ash amount, which may contribute to a higher reactivity of those fuels and therefore a higher carbon conversion. On the other hand, biochar obtained from woodchips and grass+leaves has moderate carbon content (53–56.5%), but the highest oxygen content (~13%), which is associated with the presence of oxygen-containing functional groups in the fuel matrix—the quantity of the surface oxygen functional groups directly affects the electrochemical discharge rate of carbon fuels in the DCFC [17,36,37].

3.1.2. FTIR Analysis

The FTIR spectra of all examined biochar are shown in Figure 7 and the FTIR wave number identification was summarized in Table 3. In all tested samples, a wide band in the range 2800–3600 cm^{-1} (peak centre located at 3400 cm^{-1}), attributed to –OH stretching vibration groups in alcohols, phenols and carboxylic acids (or may be attributed to vibration in hydroxyl group derived from the water molecules absorbed by carbon material during the grinding of KBr and preparation of the pellets), was observed. Moreover, a band number between 1550 and 1680 cm^{-1} (peak centre located at 1600 cm^{-1}) and 1350–1460 cm^{-1} (peak centre located at 1430 cm^{-1}), which were assigned to C=C and C-H stretchings, respectively, were also present in the spectra of all biochar. The wide peak located at wave number 1430 cm^{-1} can be also attributed to C–O–H bending vibrations of carboxyl group. A band at 1086 cm^{-1} may be assigned to C–O–C stretching vibration of cyclic ethers and the stretching vibration of C–O groups in alcohols, phenols, esters and carboxylates. On the other hand, Si–O–Si stretch has a strong, broad IR band in the 1000–1100 cm^{-1} region with peak centre around 1080 cm^{-1}. Taking into account the results of ash and oxygen content in the tested biochar (Table 2) and recorded FTIR spectra (Figure 7), the peak located at 1086 cm^{-1} should be assigned to the Si–O–Si stretch band. The band at 875 cm^{-1} clearly observed in the woodchips and sewage sludge FTIR spectrum was assigned to calcite. Generally, the more ash in the sample, the more the pronounced peak located at the wave number 1086 cm^{-1}, while the more oxygen contained in the biochar, the more the pronounced peak at 1430 cm^{-1}.

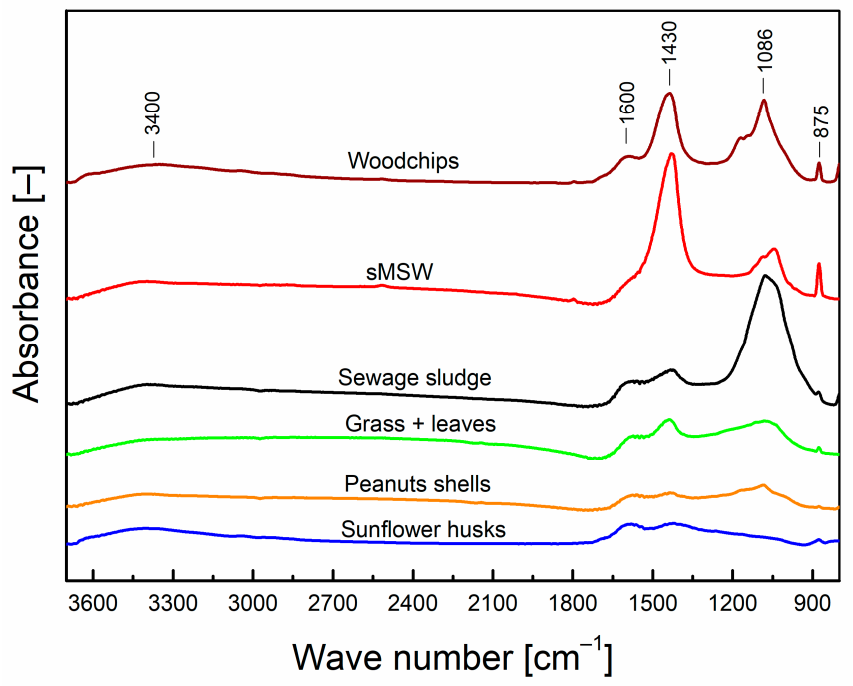


Figure 7. Averaged FTIR spectra of the carbonized organic waste.

Table 3. FTIR absorption bands present in the spectra of tested carbonized organic waste.

Wavenumber of Absorbance —Peak Centre (cm^{-1})	Wavenumber of Absorbance —Zone Range (cm^{-1})	Corresponding Functional Groups (KnowItAll® Database)
3400	2800–3600	–OH
1600	1550–1680	C=C
1430	1410–1480 1350–1460 1430	–OH C–H Si–C_6H_5
1086	1050–1130	C–O–C or Si–O–Si
875	840–880 780–980 875	N–O C–H $CaCO_3$

3.1.3. SEM/EDX Analysis

The SEM/EDX analysis of the individual carbonized organic waste samples is given in Figure 8. As can be seen, the surface morphology of these materials is exceptionally diverse. Notably, there is the presence of an amorphous carbon phase in relation to the inorganic condensed phase, as demonstrated in Figure 8b,f. The biochar structure encompasses a broad spectrum of minerals and organic substances. Additionally, porous structures are evident, featuring various shapes, including elongated forms, oblong grains, spheres, and even shapeless particles. Different sizes and shapes of biochar particles can be influenced by the type of waste used as well as steps of sample preparation, such as grinding and sieving. Additionally in some photos the macropores and even wider mesopores are seen quite clearly (Figure 8b,d–f). It can be pointed out that the resulting porous structure favours the use of biochar in MH-DCFC due to the increased electroactive surface of the electrode. On the other hand, the rougher surface of the biochar particles could reduce the contact between the fuel and the current collector.

The energy dispersion X-ray spectroscopy (EDX) of different biochar samples indicated that the some biochar types have more minerals (e.g., sewage sludge and sMSW), which can be correlated with high ash content (see Table 2). Regarding the biochar from

sunflower husks, grass+ leaves, woodchips and peanuts shells, as presented in Figure 8, it is noteworthy that the element identified in larger quantities was carbon (69.5%–83.4%), which can be correlated with high elemental carbon content (see ultimate analysis data in Table 2). Other elements were also identified including oxygen, calcium, magnesium, potassium and sodium. In the case of the woodchips (Figure 8b), spectrum 1 clearly shows that there are also grains of the mineral substance among the biochar particles.

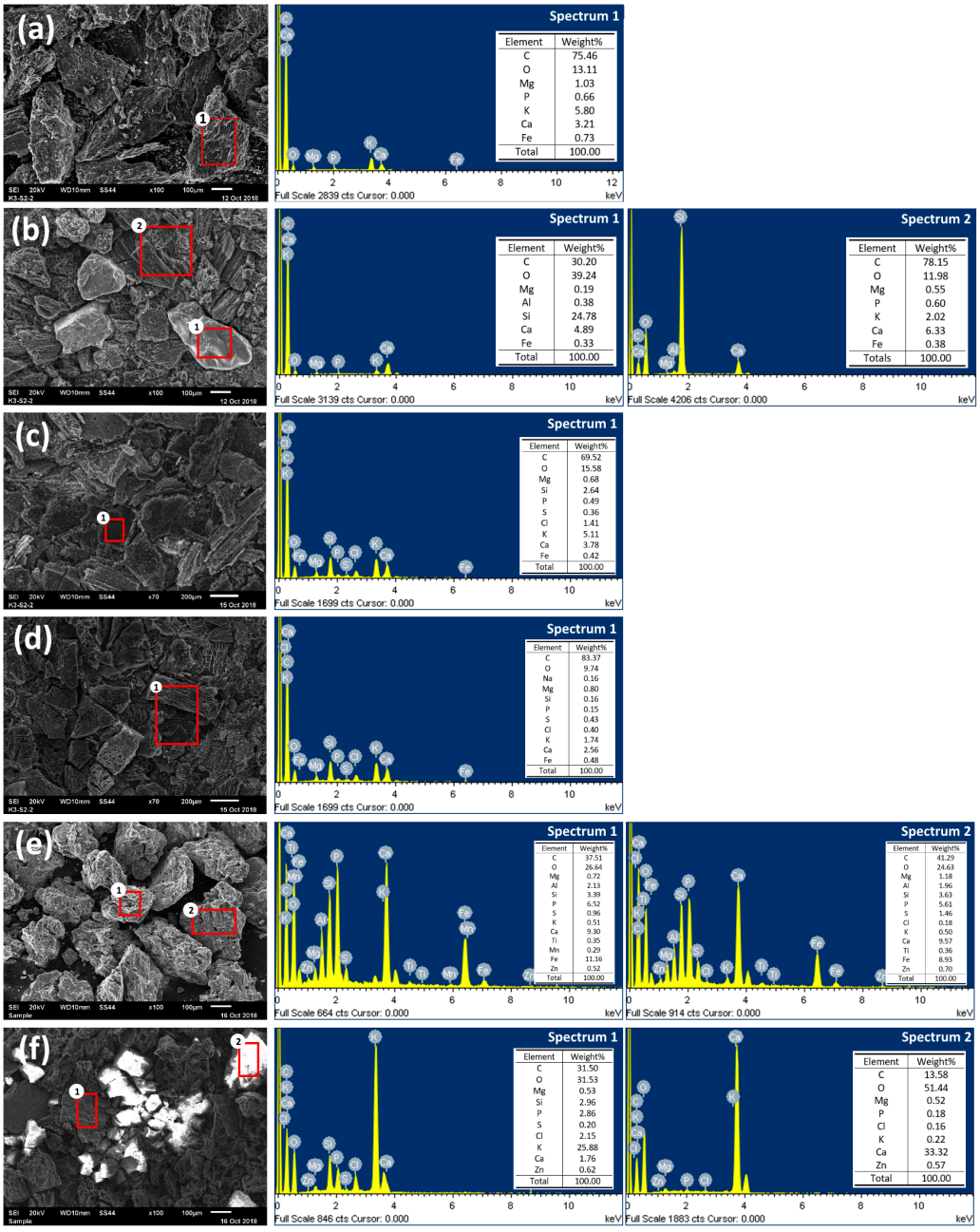


Figure 8. Scanning electron micrographs (SEM) and EDX spectrograms of different biochar samples: (**a**) sunflower husks, (**b**) woodchips, (**c**) grass+ leaves, (**d**) peanuts shells, (**e**) sewage sludge, (**f**) sMSW.

3.1.4. XRD Analysis

Figure 9 presents the XRD patterns of the carbonized waste samples. XRD patterns have been extensively used to determine the level of carbonization (pyrolysis) and to characterize the inorganic compounds present in the biochar structure. The broad hump in the region 15°–30° indexed as (002) in the biochar samples obtained from grass+ leaves, wood-

chips, sunflower husks and peanuts shells (Figure 9a–d) could be assigned the stacking structure of aromatic layers, and the broadening has originated from the small dimensions of crystallites perpendicular to aromatic layers. Similarly, another broad hump in the region 40°–50° visible in biochar from woodchips, sunflower husks and peanuts shells (Figure 9a–c) is due to crystal plane index of (100). This (100) peak is due to condensed aromatic carbonized planes. Thus, peaks depict the appearance of a degree of crystalline orientation of C in biochar samples. As expected, sharp and intense signals attributed to minerals were observed in several biochar samples that also contained higher inorganic content. Quartz (SiO_2), calcite ($CaCO_3$), magnetic iron oxide (e.g., magnetite; Fe_3O_4) and dolomite ($CaMg[CO_3]_2$) were common features in the analysed samples (Figure 9c–f). The presence of kalicinite ($KHCO_3$) was also observed for three biochar samples (Figure 9d–f). Fuels with the lowest ash content (sunflower hulls and peanut shells; see Table 2) did not show peaks corresponding to, e.g., SiO_2, $CaCO_3$ or Fe_3O_4, which were visible in the case of other high ash content carbonized organic waste.

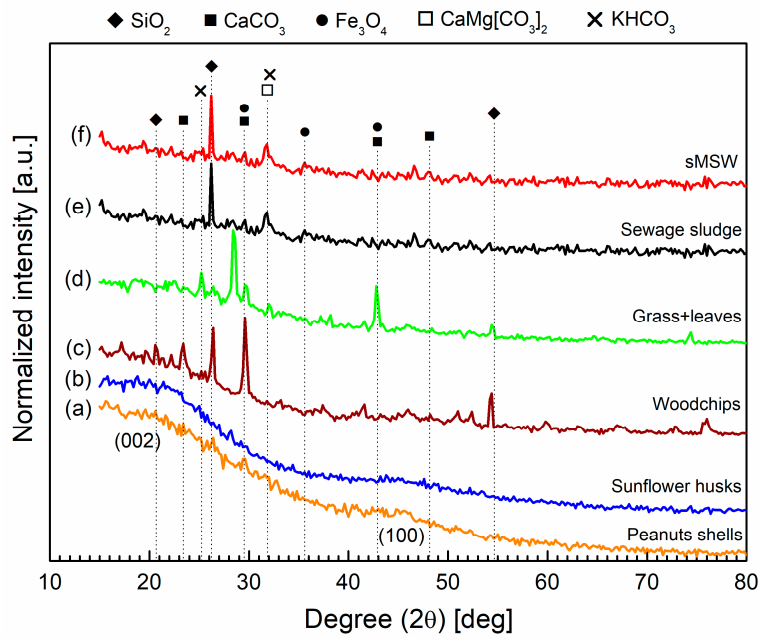


Figure 9. XRD patterns of carbonized organic waste.

3.2. Evaluation of Organic Waste Delivered Fuels (Biochar) in the MH-DCFC

3.2.1. The Effect of Organic Waste Type on Cell Voltage

The biochar samples, derived from the pyrolysis of organic waste materials, were prepared to assess their electrochemical conversion in the MH-DCFC. Figure 10 displays the changes in cell voltage over time for a current of I = 0 A. The experimental findings for the Open Circuit Voltage (OCV), measured using a digital multimeter and data acquisition system after 3 h of continuous cell operation, are presented in Table 4.

Table 4. Open circuit voltage (OCV) for various fuel samples measured after 3 h of continuous operation of the MH-DCFC.

Fuel Sample	Sunflower Husks	Peanuts Shells	Grass + Leaves	Woodchips	Sewage Sludge	sMSW
OCV [V]	1.0172 ± 0.0008	1.0105 ± 0.006	0.9460 ± 0.0024	0.9839 ± 0.0011	0.9765 ± 0.0010	1.0602 ± 0.0007

In all cases, the cell voltage exhibited a gradual increase until it reached a stable *plateau* after approximately 2 h, remaining relatively constant thereafter. Differences in the OCV values, particularly during the initial period of around 0.5 h, were likely a result of

the progressive wetting of the inner surface of the biochar particles by the liquid molten electrolyte [17].

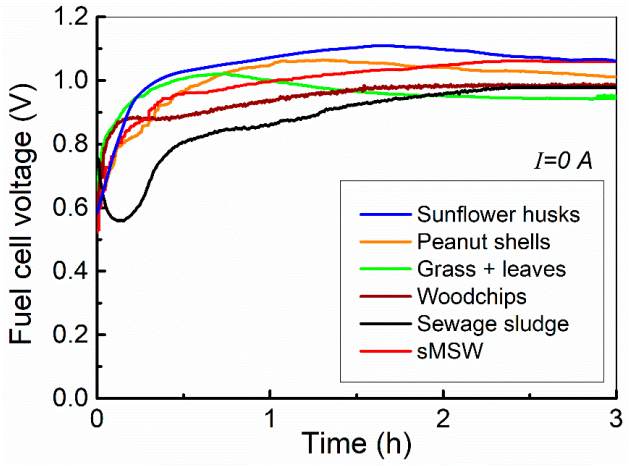


Figure 10. The variation of the fuel cell voltage vs. time for the current $I = 0\ A$.

The highest OCV values were recorded for sMSW, while the least favourable results were obtained for grass+ leaves. Sunflower husks and peanut shells exhibited similar OCV values, approximately 1.0 V. It is worth noting that the experimental OCV values for sMSW exceeded the theoretical standard potential of 1.025 V [17]. A higher OCV value suggests the occurrence of additional reactions beyond the direct electrochemical oxidation of carbon to CO_2. One possible explanation may be related to the chemical composition of the waste and the presence of impurities in the ash that can undergo chemical oxidation at the fuel cell's anode. Alternatively, the elevated OCV could be attributed to an increased number of available active sites, indicating greater chemical activity of the fuel. Nevertheless, this phenomena requires further research work.

3.2.2. The Effect of Organic Waste Type on Current and Power Densities

Figure 11 presents the potential–current density (I-V) characteristics while Figure 12 shows the power density–current density (I-P) profiles of the MH-DCFC fuelled by carbonized organic waste. The main operation parameters of fuel cells are summarized in Table 5.

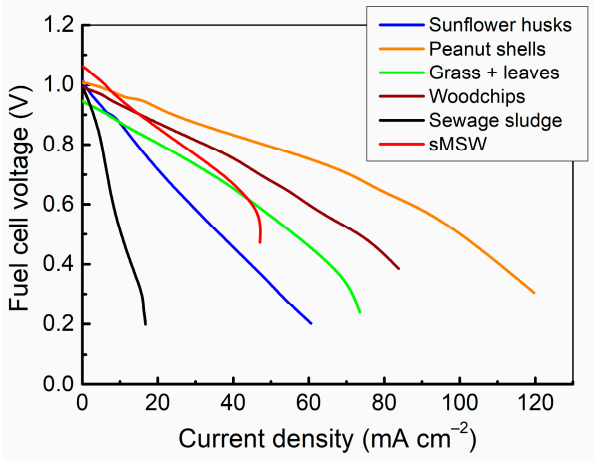


Figure 11. Cell voltage vs. current density for the examined MH-DCFC.

As indicated by the results presented in Figure 11, the current–voltage characteristics of the examined MH-DCFC are primarily influenced by ohmic losses, encompassing electrolyte resistance, current collector resistance, and carbon resistivity. A comparison of the polarization curves for different fuels indicates no significant impact of activation

polarization. The recorded values ranged from 16.8 mA cm^{-2} to 119.8 mA cm^{-2} and were contingent on the type of fuel. The most promising results were obtained for carbonized peanuts shells (119.8 mA cm^{-2}) and pyrolyzed woodchips (83.8 mA cm^{-2}). In order to compare the current densities at similar voltages for all the tested fuels, it was decided to present the data for 0.7 V (see Table 5). In the case of charred grass + leaves and sMSW, the current densities at 0.7 V were similar: 34.41 mA cm^{-2} and 37.07 mA cm^{-2}, respectively. The lowest value was obtained for a sewage sludge (6.46 mA cm^{-2}). In turn, the highest value was obtained for MH-DCFC supplied by peanuts shells (70.72 mA cm^{-2}).

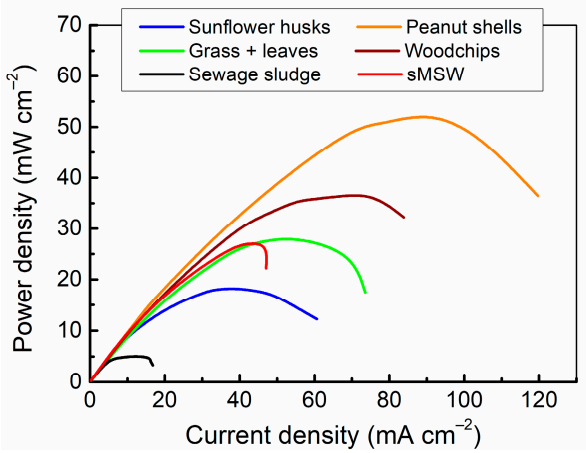


Figure 12. Power density vs. current density for the examined MH-DCFC.

Table 5. Summary of the main operation parameters for MH-DCFC.

Fuel Sample	Maximum Power Density	Maximum Current Density	Current Density at 0.7 V
	[mW cm^{-2}]	[mA cm^{-2}]	[mA cm^{-2}]
Sunflower husks	18.35	60.63	20.92
Peanuts shells	53.14	119.77	70.72
Grass + leaves	27.97	73.53	34.41
Woodchips	36.80	83.82	47.10
Sewage sludge	5.12	16.76	6.46
sMSW	27.25	47.06	37.07

The maximum power density made up 53.1 mW cm^{-2}. The lowest value was determined for sewage sludge (5.1 mW cm^{-2}), while the best results were obtained for peanuts shells. Similar values were obtained for Grass + leaves and sMSW, 27.97 and 27.25 mW cm^{-2}, respectively.

The highest value of power density was obtained for carbonized peanut shells, which is related to the high content of both fixed carbon (FC) and elemental C, as well as a small content of ash (see Table 2 and Figure 8d). Moreover, this fuel was characterized by low oxygen content, which is part of, among others, surface oxygen functional groups in the molecular structure of biochar (see Figure 7), which influences the reactivity of the fuel. It can therefore be concluded that the high proportion of elemental carbon (the main substrate for electrochemical reactions taking place at the anode of the cell) had the greatest impact on the performance of the cell in the case of this fuel.

The second highest value of power density (36.8 mW cm^{-2}) was obtained for woodchips, which was characterized by a higher ash content and lower content of carbon and FC in comparison with peanut shells. In this case, the oxygen content is the highest among all the carbonized waste (see Table 2 and Figure 7), which, despite the high ash content, was probably of key importance for the reactivity of this fuel and obtaining the second highest power density among all other organic waste. It is also worth noting that in the

case of sMSW it is clearly visible that the high level of oxygen in the fuel structure also had an impact on obtaining a relatively high reactivity of the fuel (determined by the power density value) despite the high content of mineral substances. Grass + leaves were also characterized by a high ash and oxygen content, which mainly contributed to obtaining a similar value of power density as in the case of sMSW despite the lower content of the elemental carbon. The results obtained for sunflower husks also require discussion. They indicate that in this case, despite the highest carbon and the lowest ash content, the second lowest power density value was obtained. This result was probably influenced by the low content of oxygen (see Table 2), which was not part of the reactive oxygen-containing groups present in the biochar surface (see Figure 7), but formed potassium and calcium oxides (see Figure 8a).

The lowest power density values were recorded for sewage sludge, which had the highest ash content among all the tested fuels, with the lowest content of carbon and oxygen. It was believed that the ash, which is mainly from silica (Figure 9) and iron (Figure 8e), acted as a barrier for the carbon to be in contact with the anode current collector, and thus severely blocked the active sites of the anode for oxidation.

3.3. Comparison Results and Discussion

The main characteristics, performance key factors and operating conditions of the different DCFCs developed in the world using various forms of organic waste as fuel are pointed out in Table 6.

Table 6. Direct carbon fuel cells performances using various forms of organic waste as fuel.

Organic Waste Type/ Source of Biochar	DCFC Type	Working Temperature	OCV	Maximum Power Density	Maximum Current Density	Ref.
		[K]	[V]	[mW cm^{-2}]	[mA cm^{-2}]	
Sunflower husks	MH-DCFC	723	1.02	18.35	60.63	This work
Peanuts shells	MH-DCFC	723	1.01	53.14	119.77	This work
Grass+ leaves	MH-DCFC	723	0.95	27.97	73.53	This work
Woodchips	MH-DCFC	723	0.98	36.80	83.82	This work
Sewage sludge	MH-DCFC	723	0.98	5.12	16.76	This work
sMSW	MH-DCFC	723	1.06	27.25	47.06	This work
Corn cob	H-DCFC [1]	873 1023	≈0.9 1.05	≈35 185	≈150 ≈500	[21]
Almond shell	H-DCFC	1023	1.07	127	480	[22]
Olive wood	H-DCFC	873 973	≈1.0 1.02	≈32 105	≈125 550	[38]
Waste coffee grounds	SO-DCFC	1023 1173	≈0.93 ≈1.03	≈55 87.2	≈115 ≈260	[20]
Wheat	SO-DCFC	873 1073	0.87 1.18	2.8 66.92	17.68 138.52	[30]
Spruce	SO-DCFC	873 1073	0.37 1.16	1.34 57.4	13.26 156.2	[30]
Palm kernel shell	SO-DCFC	1123	0.8	3.3	≈7.8	[39]
Mesocarp fibre	SO-DCFC	1123	0.89	11.8	27.1	[40]
Rice husk	SO-DCFC	1123	0.92	135	140	[41]
Peach pit (activated carbon)	MC-DCFC	1073	≈1.18	84	124 (at 0.8 V)	[42]
Coconut (activated carbon)	MC-DCFC	1073	≈1.22	56	102 (at 0.8 V)	[42]

[1] H-DCFC—Hybrid Direct Carbon Fuel Cell (mixed solid oxide and carbonate electrolyte).

A wide variety of biomass feedstocks are used as fuel in DCFCs, as shown in Table 6. The power output of a DCFC is strongly affected by the working temperature (fuel cells operating at higher temperatures achieved higher power density values). Moreover, typical power densities achieved from different types of DCFCs do not exceed 200 mW cm^{-2}. Among all organic waste types listed in Table 6, the highest power density was obtained for corn cob biochar (185 mW cm^{-2}).

4. Conclusions

The direct carbon fuel cell (DCFC) is a power generation device converting the chemical energy of carbon directly into electricity by electrochemical oxidation of the fuel, without the combustion, gasification process or the moving machinery associated with conventional heat engines. The basic structure of a DCFC is identical to any of the other fuel cells. It is similar in operation to typical MCFC or SOFC technologies. However, it uses solid carbonaceous fuels (e.g., hard coals, charred biochar, active carbons, carbon black, graphite, coke, etc.) directly at the anode surface in place of gaseous fuels (e.g., H_2 or CO).

In this paper, the DCFC with molten hydroxide electrolyte (MH-DCFC) was examined. Organic wastes from different origins (food processing industry, urban and sub-urban areas, municipal solid organic waste, sewage sludge) with diversified characteristics were employed as the main feedstock for tested MH-DCFC and the following conclusions are obtained:

1. The highest OCV values were observed for sMSW, while the least favourable outcomes were obtained for Grass+ leaves. The OCV values for sunflower husks and peanut shells were approximately 1.0 V. It is noteworthy that the experimental OCV values measured for sMSW surpassed the theoretical standard potential of 1.025 V. A higher OCV value suggests the occurrence of additional reactions beyond the direct electrochemical oxidation of carbon to CO_2. One potential explanation may be linked to the chemical composition of the waste and the presence of certain impurities within the ash, which could also undergo chemical oxidation within the cell. Alternatively, the elevated OCV might be attributed to an increased number of available active sites, indicating a higher chemical reactivity of the fuel.
2. Among the tested fuels, carbonized peanut shells provided the highest power density of 53.1 mW cm^{-2} because of the low ash and high carbon content. Despite the high carbon and the low ash content, the power density value for carbonized sunflower husks was not as high as expected because of the low content of reactive oxygen-containing groups present at the biochar surface. Moreover, MH-DCFC directly fuelled with sewage sludge achieved the lowest current and power density values.
3. Generally, the higher elemental carbon, lower ash content, and the presence of a reactive surface oxygen functional group in examined pyrolyzed organic waste might contribute to the better cell performance.
4. The research study establishes the potential of carbonized organic waste as a prospective alternative fuel source for power generation in a MH-DCFC.

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