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Operation Of Solid Oxide Fuel Cells (SOFC) with Biogas Generated from Agri-Food Waste: Optimisation of Biogas Production and Analysis of Cell Performance

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Due to the internal reforming that takes place in solid oxide fuel cells, they can operate with the (bio)methane contained in the biogas produced by anaerobic digestion (AD) from organic waste. In this sense, the potential of agri-food waste (onion skins) for biogas production and its use in SOFCs has been analyzed. For this purpose, physical, chemical, thermal, and combined pretreatments were tested on onion skins to increase the anaerobic biodegradability. The evaluated pretreatments increased the soluble chemical oxygen demand (SCOD). However, it was observed that the use of $Ca(OH)_2$ was preferred to NaOH, because it allowed the precipitation of sulphates, blocking the biological production of H_2S, which acts as a toxic compound for methanogenic archaea and as a catalytic poison of SOFC systems. This combination of pretreatments increased methane production by 36 and 19 % compared to untreated substrate. Once the most suitable pretreatment was identified, the biogas produced was used to feed a SOFC optimized by advanced ceramic processing to operate with this biofuel. The electrochemical performance of SOFC was examined through the characterization of I-V-P and EIS curves for H_2 and the obtained biogas as fuels, operating at different temperatures: 800, 850, and 900 °C. Power densities were only reduced by 18 – 35 % when biogas was used instead of H_2.

1. Introduction

Onion is a major agricultural product responsible for 500,000 tons of annual waste in just the European Union, which can create harmful effects on people's health and the environment (Sagar et al., 2022). To minimize onion waste, some studies related to the extraction of antioxidants like quercetin, production of dietary fiber, production of ethanol, and production of biogas through anaerobic digestion process were carried out (Domínguez-Maldonado et al., 2020). Biogas produced through AD is energy efficient and environmentally friendly, as it can replace fossil fuels to produce heat and power. AD is a microbiological process that involves four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The rate-limiting step depends on the substrate type. In this sense, the hydrolysis phase can be the rate-determining step when microorganisms do not produce enough hydrolytic enzymes to break down the highly complex substrates such as lignocellulosic ones, which is one of the main components of onion skin. To favor the hydrolysis of onion waste by breaking down the lignin structure, some pretreatment methods can be applied as mechanical, thermal, chemical, biological, or a combination of them. Pretreatment decreases particle size, simplifies composition, and helps its solubilization, making the compounds contained in the onion more accessible to the microorganisms involved in AD (Atelge et al., 2020). However, pretreatment conditions need to be set to not produce inhibitory compounds (Surra et al., 2018).

On the other hand, electricity from biogas could be produced using fuel cells, which convert the chemical energy of fuels into electricity with high efficiency. In particular, high-temperature fuel cells such as SOFCs can be fed with complex fuels such as biogas which is converted to electricity by a direct internal reforming, in which, first methane reacts with CO_2 and converts it into CO and H_2, and then electrical energy is produced through the subsequent exothermic electrochemical oxidation of H_2 and CO (Abdelkareem et al., 2019).

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The combined system AD-SOFC is an attractive alternative for waste treatment, heat and electricity generation, and fertilizer (digestate) production. Biogas production could be a carbon-neutral process since it is produced from waste. Moreover, the AD-SOFC system avoids the emission of greenhouse gases. It was used in wastewater treatment plants (WWTP) achieving a reduction in CO_2 emissions of 3,5 $KgCO_2$/person (Grasham et al., 2019). Lackey et al. (2017) achieved a reduction of 432 tCO_2/d in their simulation using a SOFC fed with biogas in a WWTP and 130 tCO_2 eq were saved in AD-SOFC-micro CHP using the organic fraction of municipal solid waste (Evangelisti et al., 2015).

The present study focuses on the valorization of onion skin obtained during the onion production process by AD. For this purpose, different pretreatments of this waste were evaluated to optimize and maximize methane production to use it as a fuel for SOFC. Electrochemical measurements were performed and analyzed to study the influence of biogas in SOFC.

2. Materials and methods

2.1 Feedstock composition

Onion skin waste was produced by Quirosa Cebollas S.L. (Ciudad Real). The main features were 41.3 % of Total solids (TS), 38.4 % of volatile solids (VS), 0.59 % of total Kjeldahl nitrogen (TKN), 3.75 % of proteins, and a pH of 4.5.

2.1 Feedstock conditioning for anaerobic digestion

Onion skin (20 gSV/L) was pretreated using different methods. In the mechanical pretreatment, a coffee grinder was used to decrease the particle size and increase the bioavailability of the substrate. Two procedures were followed for the thermal treatment. On the one hand, the sample was pre-dried at 37 °C to facilitate milling. On the other hand, a hydrothermal pretreatment was performed. In the former, low temperatures (25, 37, and 70 °C) were selected to reduce the costs related to energy requirements and to avoid the generation of inhibitory compounds at high temperatures. NaOH and $Ca(OH)_2$ (5 and 10%) were chosen for the chemical treatment because alkaline hydrolysis can reduce the lignin content, making cellulose and hemicellulose available. In this case, different exposure times (1, 4, and 24 h) were studied to assess the influence of this variable. The effectiveness of the conditions assayed was assessed through SCOD. Sulphates (SO_4^{2-}) were also determined at the end of the alkaline pretreatment.

2.2 Biochemical Methane Potential (BMP)

Inoculum was taken from the anaerobic digestion reactor (35 °C) of the WWTP located in Ciudad Real. The features of the inoculum used were: pH 7.6, 4.3 % TS, and 2.8 % VS. The BMP test was performed according to Holliger et al. (2016) under mesophilic conditions (37 °C). The inoculum:substrate ratio (ISR) was 1 and the substrate concentration was 20 gVS/L when onion skin was pretreated with NaOH and 10 gVS/L were added when $Ca(OH)_2$ was used. The BMP assays were run for 60 d. To quantify the biogas production a manometric method was used, and to determine its composition (CH_4, CO_2, H_2, and H_2S) a gas micro-chromatograph with a thermal conductivity detector was utilized.

2.3 Cell fabrication

Reversible solid oxide cells of circular geometry supported on electrolyte were used for the electrochemical characterization. For the manufacture of the YSZ electrolyte, a tape casting process was used, obtaining an electrolyte thickness of 200 microns. The deposition of the cathodic layer (NiO-YSZ), the anodic layer (LSM), and the barrier layer (GDC) were carried out by ultrasonic aerography with a Cheersonic UAM4000L equipment, adjusting the layer thicknesses by 20 microns for the electrolyte layers and by 2 microns for the barrier layer. Figure 1 shows the thickness distribution and dimensions of the cells: 50 mm external diameter with an electrode active area of 36 cm^2.

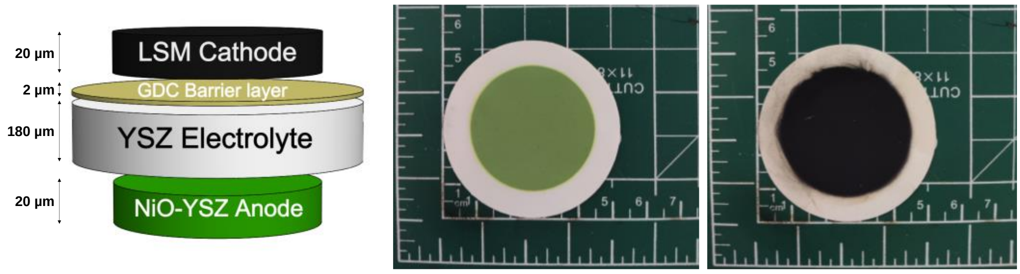

Figure 1. Features and dimensions of the cells used.

2.4 Electrochemical test

To carry out the electrochemical test, Pt paste was used in the cathode and anode to enhance the contact between the cells and Ni and Au collectors. The cells were mounted on an Open FlangesTM Test Set (Fiaxell) attached by a spring-loaded mechanism. Then, to separate the anode and cathode chambers, Mica Phlogopite Paper was used as a sealant. Electrochemical measurements were collected using a Potentiostat/Galvanostat VSP (Biologic) coupled to a Booster VMP3 (Biologic), using H_2 (3 vol% H_2O) and a mix of CH_4/CO_2 (50/50 % vol) as fuels gas on the anodic side and air on the cathodic one at temperatures of 700, 750, 800, 850 and 900 °C. The flow rates were set at 12 L/h for each fuel individually, H_2 and biogas, and 6 L/h for air.

2.5 Analytical methods

TS, VS, SCOD, and SO_4^{2-} concentrations were analyzed according to APHA Standard Methods (1992). Protein content was determined by total nitrogen Kjeldahl (NTK) (A.O.A.C. Official Methods of Analysis, 1980), multiplying the NTK by 6.25 (Allen, 1974).

3. Results and discussion

3.1 Feedstock pretreatment and BMP test

The effects of different pretreatment on onion skin in terms of SCOD are shown in Figure 2.

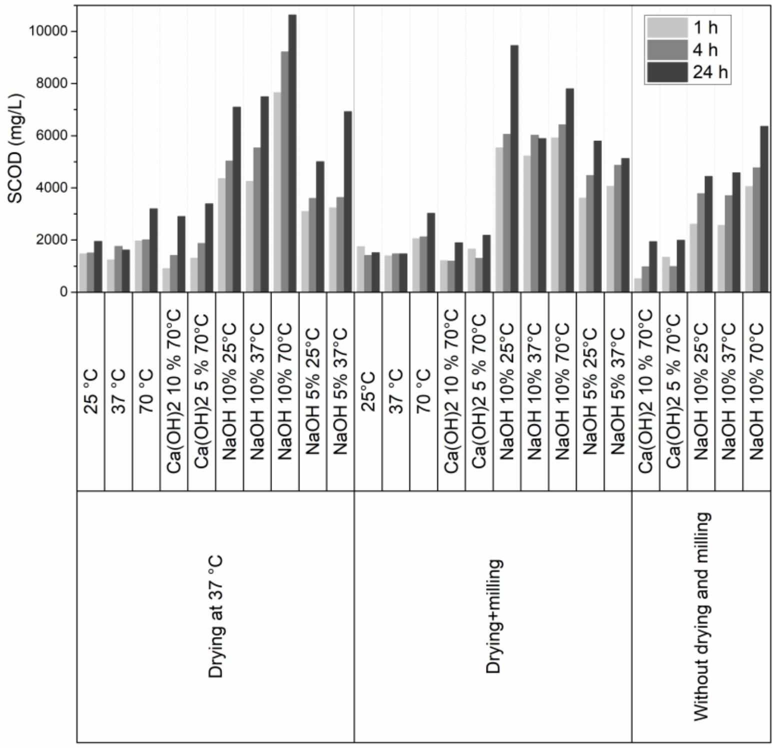

Figure 2: Effects of the different pretreatments studied on the SCOD (mg/L) of substrate tested.

The data indicate that pretreatment temperature and its length increase the SCOD significantly because of the degradation and dissolution of insoluble organic compounds such as carbohydrates, lipids, and protein (Ahmed et al., 2021). The highest SCOD values were reached only with a pre-drying step since evaporation of soluble organics could occur during the milling process. Increasing alkaline load increased SCOD when Na(OH) was used. The hydrolysis ability of bivalent alkali ($Ca(OH)_2$) was lower than monovalent alkali (NaOH), since the bivalent alkali agent (Ca^{2+}) could re-flocculate with proteins under alkaline conditions, decreasing protein hydrolysis (Jin et al., 2016), and could combine with the organic matter forming insoluble compounds and decreasing the SCOD (Linyi et al., 2020). This phenomenon could also explain the decrease in SCOD when $Ca(OH)_2$ concentration was raised. The highest SCOD values (4055-10630 mg COD/L) were achieved with a pre-drying (37 °C) phase and using an alkaline hydrolysis with Na(OH) (10%) at 70 °C for 24 h. Therefore, this pretreatment was selected as the first choice for the performance of BMP test. Figure 3.a depicts the cumulative methane produced from onion skin pretreated with NaOH (10%, 70 °C, 24h) during the BMP test. As it is shown, the selected pretreatment negatively impacted the AD process, since a high H_2S concentration (10%) was detected, due to SO_4^{2-} solubilization when onion skin was pretreated with Na(OH). High SO_4^{2-} concentration promotes the growth of sulphate-reducing bacteria (SRB) which compete with methanogenic archaea for the available substrate. In addition, SRB use SO_4^{2-} as an electron acceptor, transforming it into H_2S, which is an inhibitory compound for the microorganisms involved in AD, but especially for methanogenic ones. To decrease the concentration of SO_4^{2-}, $Ca(OH)_2$ (5%, 70 °C and 24h) was chosen as a pretreatment. In this case, the SCOD achieved after the pretreatment was lower compared to Na(OH), but the concentration of SO_4^{2-} was below 200 mg/L. BMP tests (Figure 3.b) showed a higher CH_4 production than in the previous case, reaching 495 $mLCH_4$ when cut and dry onion was used, followed by dry onion (436 $mLCH_4$). The methane production was increased by 36 and 19 % compared to untreated substrate (365 $mLCH_4$). Similar results were found by Zhang et al. (2020), which improved biogas production between 23 and 35 % when using $Ca(OH)_2$ as a pretreatment on waste sludge. Mustafa et al. (2018) also increased methane yield by 61 % using a combined pretreatment with $Ca(OH)_2$ for the AD of sugarcane bagasse. Maximum biogas production (566 mL) from wheat straw was found when it was pretreated with 10 % $Ca(OH)_2$ (Rani et al., 2021). When a substrate is a refractory waste, calcium-containing alkaline substances can modify the surface structure of the substrate, reduce the lignin and cellulose or hemicellulose content, or release soluble organic matter (Yang et al., 2021) improving the AD process. The composition of the biogas produced in the tests with $Ca(OH)_2$ was independent of the pretreatment combination applied, being the same in all cases (50% CH_4 and 50 % CO_2).

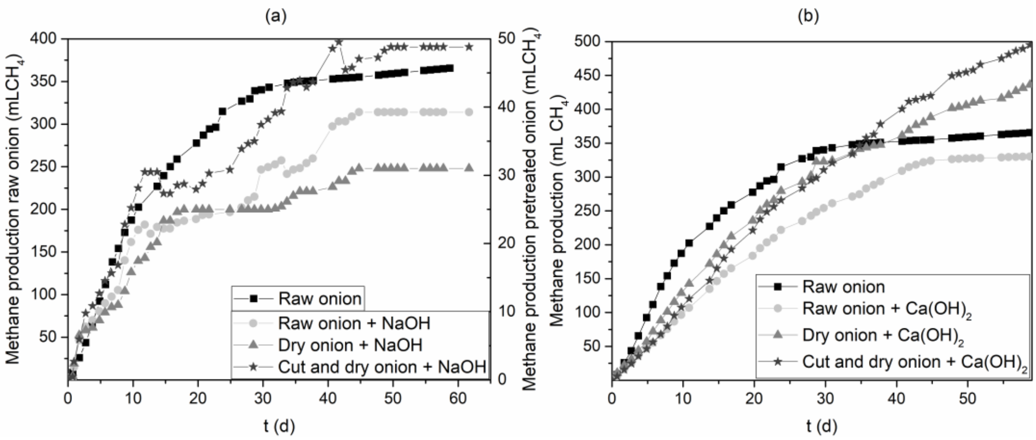

Figure 3: Time-evolution of CH_4 production during BMP test using Na(OH) (a) and $Ca(OH)_2$ (b).

3.2 Cell electrochemical characterization and fabrication.

The Current-voltage and current-power characteristics of cells at 800, 850, and 900 °C are given in Figure 4. The obtained open circuit voltage (OCV) was predicted by the Nernst Equation (1.10 V at 750 °C). In Figure 4, it was observed that the OCVs for H_2 and biogas at different temperatures were similar to the one calculated by the Nernst equation. It can be noticed that an increase in temperature significantly affects electrochemical properties, decreasing the resistance (Table 1), and as a consequence, increasing the output power density. It can be seen that maximum power densities fueling H_2 at 800, 850, and 900 °C were 75.22, 136.15, and 198.57 $mW{\cdot}cm^{-2}$, respectively. When biogas was used, these values were 51.04, 102.62, and 163.62 $mW{\cdot}cm^{-2}$. Figure 5 shows, for each temperature, the EIS diagram for H_2 and CH_4/CO_2. A trend was observed: when the temperature increases, the values of real Z-axis decrease. This means that the ohmic drop, the activation of the electrodes as well as the diffusion processes, are thermally activated. From the EIS spectra it is possible to obtain total resistance, value that include ohmic and polarization resistances, which can be obtained from the intersection of the diagram with the Z real axis in the low frequencies zone. Total resistances decreased when the temperature increased from 5.15 to 1.41 Ω*cm^2 when H_2 was used, and from 5.65 to 1.66 Ω*cm^2 when biogas was fed. Biogas resistance increases by 10-23% since CH_4 molecules' diffusion is not as easy as the H_2 ones and due to the internal reforming of CH_4. The decrease in ohmic resistance could be related to carbon deposit formation, which can enhance the electronic conductivity and increase the active area (Escudero et al., 2022). The arc size decrease also means an increase in total conductivity as a result of the pure electronic conduction behavior of nickel (Rafique et al., 2019). These electrochemical tests revealed that the power density decreased when SOFC was fed with CH_4/CO_2 instead of H_2. Liu and Barnett (2003) related that phenomenon to the higher mass of methane molecules, which yields slower gas-phase diffusion and increased concentration polarization, and to a higher polarization resistance as methane oxidation is not as fast as the H_2 one.

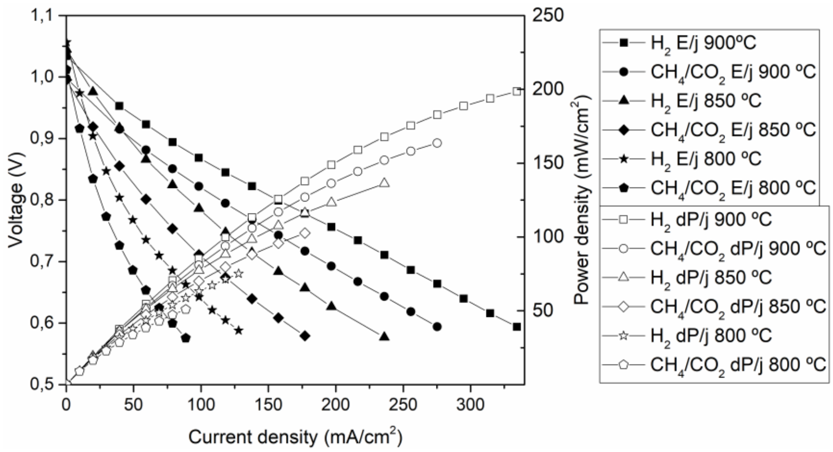

Figure 4: (I-V-P) curves of cells for H_2 and CH_4/CO_2 (50/50 % vol) at 800°C, 850°C, and 900°C (solid symbol on the left axis (Voltage, V) and open symbols on the right axis (Power density, mW/cm^2)).

Table 1: Maximum power density and total resistance obtained at different temperatures.

Temperature (°C)	Fuel composition	Maximum power density (mW*cm^{-2})	Total resistance (Ω*cm^2)
800	H_2	75.22	5.14
	CH_4/CO_2	51.04	5.65
850	H_2	136.15	2.43
	CH_4/CO_2	102.62	3.00
900	H_2	198.57	1.41
	CH_4/CO_2	163.62	1.66

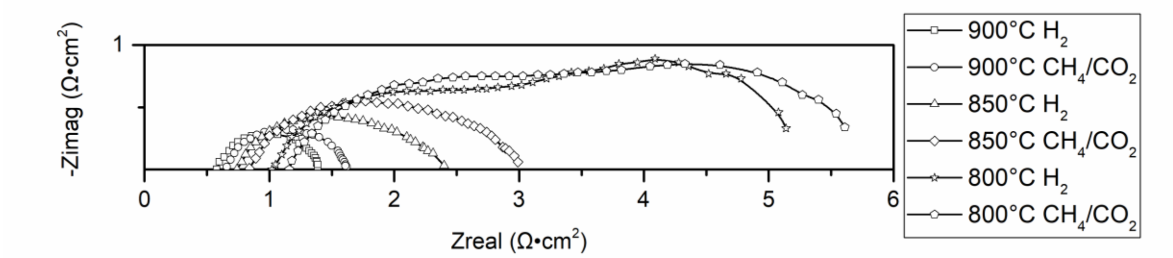

Figure 5: Nyquist diagrams for H_2 and CH_4/CO_2 (50/50 % vol) at 800°C, 850°C and 900°C.

4. Conclusions

Electrical energy can be produced from the valorization of onion waste through the production of biogas and its direct feeding to a high-temperature fuel cell such as SOFC. For this purpose, different pretreatments were assessed for improving the anaerobic digestion of onion waste. It was observed that a combined pretreatment of mechanical (grinding), thermal (70 °C, 24 h), and chemical (5 % $Ca(OH)_2$) processes showed higher methane production than other pretreatments. This methodology produced a biogas composed of CH_4 (50%) and CO_2 (50%) and improved the CH_4 production by 36 % compared to untreated substrate. The results of the characterization of the I-V-P and EIS curves verified a successful electrochemical performance using this biofuel. Electrochemical tests revealed that the power density only decreased by 18% when SOFC was fed with CH_4/CO_2 instead of H_2, working at 900 °C, making this fuel from waste an attractive alternative.

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