LANDFILL GAS ENERGY RECOVERY BASED ON MICRO-TUBULAR SOLID OXIDE FUEL CELLS

1 Jakub Pusz, 2 Roberto Bove and 2 Nigel M. Sammes
University of Connecticut,
1 Connecticut Global Fuel Cell Center
2 Mechanical Engineering Department
44 Weaver Road, Storrs, CT 06269, USA

ABSTRACT

The anode-supported tubular solid oxide fuel cell developed in this work does not have to be run on pure hydrogen, but can be run using a number of different hydrocarbons. In the present study, biogas naturally produced in the landfill of a University campus in the United States is considered as the fuel. The main issues to be addressed are the evaluation of the energy potential of this gas and the effect of the embedded pollutants on the fuel cell operation. In the present paper, the production process of the fuel cell is described and an overview of the planned activities for demonstrating the potential of the landfill gas is described.

INTRODUCTION

Due to the high operating temperature, solid oxide fuel cells (SOFCs) do not need precious metals as the catalysts. As a consequence, SOFCs do not require pure hydrogen as the fuel. The presence of carbon monoxide in the anodic gas represents a major issue for low temperature fuel cells, while for SOFC this represents additional fuel. For this reason, and due to the availability of thermal energy from the fuel cell reaction, the internal reforming of a variety of fuels has been considered as a valuable alternative to pure hydrogen (1, 2, 3).

At the present time, there is an effort in several countries to increase the use of renewable energies, alternative to fossil fuels. From a political point of view, countries such as the United States, Japan, and European state members, need to reduce their dependence on foreign oil, and the related (political and economical) instability related to this dependency. From an environmental point of view, the use of biogas drastically reduces greenhouse-gas emissions, and, if exploited with clean technologies, like fuel cells, NOx, SOx and other emissions are virtually zero. Finally, some types of biogas are naturally produced, thus they represent an available “free fuel”. The cost of the fuel, however, is usually due to the need of upgrading the quality to the requirements of the energy conversion system. Some studies and demonstration projects have demonstrated that the cost of investment of a biogas-based energy system is counterbalanced by the low (near zero) cost of operation, thus return of investment in a few years is potentially possible (4). Figure 1 illustrates the price competitiveness and stability of a direct-use landfill gas project as compared to the projected cost of natural gas (5).
In the present study, the landfill gas (LFG) produced in the landfill of the University of Connecticut campus is considered, Figure 2.

In addition to the benefits previously mentioned, the use of LFG leads to a further greenhouse gas emission reduction. The US Environmental Protection Agency (EPA) estimated that more than 50% of the methane emissions into the atmosphere come from landfill gas. Since methane produces a greenhouse effect that is about 21 times higher than CO₂, the benefits of this practice are noticeable. The gas from many landfills at this moment, even though they are equipped with a gas collection device, is simply burned with no energy recovery system, or is converted into electricity with efficiency lower than 25% (6). In this paper, the production process of the fuel cell and an overview of the planned activities for demonstrating the potential of the landfill gas are described.
The landfill place has several collecting wells (Figure 2b) where the gas composition was measured.

Table 1. Landfill Gas composition collected at six points at University of Connecticut Landfill.

|        | CH₄ (%) | CO₂ (%) | H₂O (%) | Other (%) |
|--------|---------|---------|---------|-----------|
| Well 1 | 45      | 145     | 3       | 7         |
| Well 2 | 45      | 145     | 3       | 7         |
| Well 3 | 52      | 38      | 3       | 7         |
| Well 4 | 59      | 31      | 3       | 7         |
| Well 5 | 63      | 27      | 3       | 7         |
| Well 6 | 77      | 13      | 3       | 7         |

The projection of landfill gas production was made using The Energy Project Landfill Gas Utilization Software (E-PLUS) (Figure 3) developed by the EPA’s Landfill Methane Outreach Program. E-PLUS uses default data and algorithms to determine the economic and environmental feasibility of the landfill place.

The landfill gas is naturally produced via the metabolism of organic wastes by anaerobic microorganisms. The fermentation is usually described by a simple two-phase system (7):

\[ C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2 \]  

[1]

\[ 2CH_3COOH \rightarrow 2CH_4 + 2CO_2 \]  

[2]
However, a more complex, four-step anaerobic digestion can occur (8):

a. **Hydrolysis** — transformation of non-soluble biopolymers to soluble organic compounds;

b. **Acidogenesis** — transformation of soluble organic compounds to volatile fatty acids and carbon dioxide;

c. **Acetogenesis** — transformation of volatile fatty acids to acetate and hydrogen;

d. **Methanogenesis** — transformation of acetate and hydrogen-carbon dioxide mixture to methane.

The bacteria that carry out fermentation are highly sensitive to the pH, which is supposed to be kept around 7.5 for optimum results. Additionally, the metabolic process is highly affected by the presence of oxygen and light (9). Controlled digestion may be carried out by three types of bacteria depending on temperatures: psychrophilic (10-20°C), mesophilic (20-40°C) or thermophilic (50-60°C). As the digestion processes are slower at low temperatures and thermophilic digestion occurs only when the waste is at high temperature, the optimum temperature range is 35-37°C (10).

The methane concentration can vary between 40-55% and is influenced by the landfill location, period of the year and gas collection practice (11). The remaining gas composition is carbon dioxide, nitrogen and oxygen. In case of acidification of the landfill also hydrogen and hydrogen sulphide are produced (9).

**CELL MANUFACTURING**

The fuel cell considered in this paper is an anode supported micro-tubular SOFC. The dimensions of the cell are 5.5 mm (ID), 6.8 mm (OD) and 120 mm of active length. Once the cells are manufactured, they can be grouped in Planar-Multicell-Arrays (PMA). The PMA are then stacked together to form a stack (12). Although the main goal is to run the stack and, finally, the entire system on LFG, as the first experimental campaign, only single cells, will be tested.

**Anode**

The substrate for extrusion was prepared by mixing NiO-8YSZ (50/50) (Inframat Advanced Materials) with polymer binder, carbon pore former (Vulcan XC605 by Cabot) and distilled water. The optimum concentration of carbon pore former (giving the highest porosity with acceptable mechanical strength) to the anode substrate was chosen by preparing several pellets of different compositions. The best concentration of pore former was found to be 10 vol%. The mixing process was carried out for 2 hours in a hermetically sealed chamber (Figure 4). The mixing process is one of the most important steps in tube manufacturing. Improper mixing may result in agglomeration of dry particles of powder inside the die, which affects the extrusion. After mixing, the mass was put into a ram extruder and a vacuum was applied. The extruded tube was placed in the specially fabricated tube-holder (Figure 5) and dried overnight at room temperature. After the drying process, the tubes were cut and fired at 1200°C for 2 hours.
Figure 4. Mechanical mixer SK-6 by Jaygo Manufacturing.

Figure 5. a) The ram extruder by Loomis; b) the tube holders that prevent tubes from bending during the drying process.
Electrolyte

The tubes were coated with the 8YSZ electrolyte slurry (NexTech Materials). The first layer of electrolyte was prepared by vacuum assisted dip coating. The tube was fired at 1500°C. This was followed by a second layer which was applied by brush painting and fired again at the same temperature. A 3-5 μm thin crack-free layer of electrolyte was obtained (Figure 6).

![Image of YSZ electrolyte](image)

Figure 6. SEM micrograph of NiO anode and YSZ electrolyte layer.

Cathode

A La0.8Sr0.2MnO3 (LSM) cathode ink (American Elements) was applied by brush painting and fired at 1200°C.

SINGLE CELL TESTING

The manufactured cells will be run on landfill gas and pure hydrogen for reference. As previously mentioned, the two main issues to be addressed are: estimating the energy potential of the LFG, and assessing the effect of the pollutants embedded in the fuel.

In order to evaluate the performance of a fuel cell running on LFG, without considering the impurities effect, tests will be conducted using simulated biogas, reproducing the H2, H2O, CH4 and other main LFG constituents. Starting from a reference composition, tests will evaluate the performances related to composition changes. LFG composition, in fact, is very sensitive to a variety of external factors, such as environmental temperature and humidity, and wastes composition. The effect of different steam to carbon ratios will also be investigated, in terms of cell voltage and potential carbon deposition inside the cell.

The effect of the some impurities in the anodic gas has not been fully studied in the open literature. Matsuzaki and Yasuda (13) performed a series of experiments on a Ni-YSZ cermet anode/YSZ electrolyte half cell, for different temperature and H2S concentrations. Results show that at 1023 K, the minimum concentration that produces a resistance change is 0.05 ppm. This value increases to 2 ppm when the temperature is increased to 1273 K. Additional information on the effect of some pollutants can be found in (14). Since chlorine represents a major constituent of LFG, a series of tests for the evaluation...
of the effect on the cell performance are planned. Preliminary tests will be performed on YSZ pellets, covered with NiO/3YSZ anode and LSM cathode. The YSZ pellets are prepared using a hydraulic press.

Half cell tests will allow the resistance variation for different impurity concentrations to be measured. A reference gas composition, representing the average LFG composition is provided to the cell. After introducing a small quantity of HCl, the resistance is compared to that obtained on pure fuel. Pure gas is provided to the cell again, in order to establish if the starting performance reduction can be recoverable. The gas concentration is progressively increased, until a reference resistance limit (chosen as “unacceptable” for the fuel cell) is reached. The same tests will then be performed on real cells, in order to measure the voltage variation. When a cell is running, in fact, a variety of other factors can be slightly different from those occurring in a pellet test. These results will be considered as reference for the stack and system construction. Due to the lack of data available from the open literature, additional tests will be conducted on H2S as well as other pollutants contaminated gases. Once the operating conditions as well as the desired impurities concentrations are assessed, samples of the LFG from the University of Connecticut landfill will be purified to the wanted level and used to run the cell.

CONCLUSIONS

The micro-tubular solid oxide fuel cell was manufactured to be run on landfill gas. The proposed study is based on using biogas collected at the University of Connecticut Main Campus landfill place. The energy potential of the gas as well as interference of pollutants with the anode materials will be demonstrated in the future.

ACKNOWLEDGMENT

The work was supported by the U. S. Environmental Protection Agency grant number SU831896.

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