Multi-criteria analysis of SOFCs performances integrated in circular bio-processes

Arianna Baldinelli*
Department of Engineering
Università degli Studi di Perugia, Italy
e–mail: arianna.baldinelli@unipg.it

Pablo Silva Ortiz
School of Chemical Engineering,
University of Campinas, Brazil
e-mail: pabloaso@unicamp.br
e-mail: p.silvaortiz@tudelft.nl

Rubens Maciel Filho
School of Chemical Engineering,
University of Campinas, Brazil
e–mail: rmaciel@unicamp.br

Giovanni Cinti
Department of Engineering
Università degli Studi di Perugia, Italy
e–mail: giovanni.cinti@unipg.it

ABSTRACT

Micro scale cogeneration units may find application in many bio-processes based on energy recovery from waste. For example, farms and small food factories are excellent candidates for micro-scale biogas production. To increase the energy performances of micro-scale plants, Solid Oxide Fuel Cells (SOFCs) are a promising choice. Hence, to push their development in such application cost reduction and performance durability are essential target. To this end, simplified SOFC system may be implemented, applying regulation strategies meant at limiting degradation. This work, based on experimental data, shows system analysis regarding to possible layouts: direct biogas feeding to SOFC and air-biogas feeding to SOFC. While air addition causes a decrease in performance, experimental evidence proves longer stability of performance, resulting in a good compromise between short and long-term efficiency.

KEYWORDS

Sustainability, Multi-criteria analysis, energy efficiency, biogas, SOFC.

INTRODUCTION

Aiming at the full energy autarky of small rural communities, energy conversion pathways focus on the efficient utilization of waste are of major concern. Likewise, many industrial processes dealing with food may add value to the management of bio-waste streams [1].

Hence, high efficiency biowaste-to-electricity conversion based on electrochemical processes is a promising pathway. For instance, Solid Oxide Fuel Cells (SOFCs) show a number of advantages over conventional technologies such as internal combustion engines (ICEs) [2]. In particular, SOFCs allow the system scalability down to sizes of 10-100 kWe without penalties on the electric efficiency (up to 50-55%) [3].

For this fact, SOFC systems suit the potentialities of sites eligible for micro digestion processes. This may act as springboard to open market opportunities also for the owner of small farms/industries. Nevertheless, the great burden is represented by initial costs [4] to set the whole system up.

In terms of system design, simple configurations and components requiring less maintenance favor the cost-effectiveness of the entire plant. For instance, concerning the SOFC technology, biofuel pre-treatment can hinder the techno-economic feasibility of the system. However, the option to perform direct fuel feeding to the SOFC offers new opportunities towards the realization of lean systems, which are competitive especially on micro-scale installations (i.e. on-farm biogas plants). In addition, the possibility to make the system fully independent (from both material and energy requirements) is very attractive and a strategy to limit the environmental footprint.

SOFC implementation in biogas plants

Biogas is a renewable fuel gas featuring a high share of methane, as well as high amounts of carbon dioxide. For SOFC operation, methane is a “hydrogen” carrier and it decomposes according to different paths, that can be essentially classified into:

- Reforming: endothermic reactions with a higher hydrogen yield. Reforming process, in turn, are classified in “steam” (CH_4+H_2O) and “dry” (CH_4+CO_2);
- Partial oxidation: exothermic reaction, yet a minor hydrogen yield;
- Cracking: exothermic reactions delivering hydrogen, but also undesired by-products (Carbon).

Looking at the system architecture, methane decomposition into hydrogen usually occurs upstream the SOFC in a dedicated component (i.e. catalytic reformer). On the other hand, it is possible to feed biogas directly to the SOFC, letting methane decomposition occur in the SOFC itself (for SOFC anodes contain large amounts of catalysts which promotes methane reforming in the same temperature range). This implies a different thermal balance and affects the SOFC performances. Advantages and disadvantages of both external and internal fuel processing are resumed in Table 1.

Table 1 External vs Internal Fuel processing in SOFC applications.

	External Fuel Processing	**Internal Fuel Processing**
Advantages	- the SOFC is operated on a safe fuel composition, less risk of degradation	- less components - cheaper solutions - more flexible for micro scale applications
Disadvantages	- additional component - the burden of degradation is shifted on the fuel pre-treatment - thermal integration may introduce energy losses - cost	- more risk for degradation and - shorter lifetime of SOFC - methane decomposition reactions produce high temperature gradients in the SOFC
Trade-offs		- alter inlet gas composition by oxygenated gases (CO_2, Air, Steam)

From a detailed literature survey on the topic, it emerges that, to go through the downscaling of the system, direct feeding of biogas to SOFC (after removal of sulphur compounds [5]) has risen much interest. Nonetheless, stable and durable performances are obtained thanks to the addition of oxygenated gases which favours methane decomposition in the SOFC. Biogas already carries CO2, that is a dry reforming promoter. However, cold spots at the SOFC inlet caused by the endothermicity of this reaction, have to be avoided to assure thermomechanical stability. Air addition to biogas seems a reasonable alternative for 3 reasons:

1) it improves SOFC stability by suppressing coking in Ni anodes [6];
2) it enables partial oxidation of methane, balancing the temperature variation induced by reforming reactions [7];
3) beside oxygen, also nitrogen is added. This could enhance the performance in low-current region for the improvement of OCV and contributes to the reduction of coking risk since it increases the gas space velocity, acting against the kinetic of carbon formation reactions [8].

According to the literature, the optimal dilution ratio is Air/Biogas = 0.4-1.5 – as found in [7] showing results of experiments performed on commercial cells at 800°C and in current density range 0-400 mA/cm2. Rather high Air/Biogas ratio is applicable without large loss of electrical efficiency due to the reduction of overvoltage.

In addition to the bibliographic evidence, it is recalled that under current load, the cell produces significant amount of water, initiating internal methane steam reforming reactions. In order to gain more insight on internal fuel processing, long-term tests are required.

Scope

This work aims at discussing the trade-off between higher performance and durability. Namely, two SOFC-based system layouts are analyzed, comparing the case of direct clean biogas feeding to SOFC to the case of direct feeding of a mixture of air and clean biogas. The models are based on experimental evidence for what concern the electrochemical part.

EXPERIMENTAL

Materials and methods

The system model is tuned on experimental data regarding the SOFC performance. Experiments are carried out on a commercial anode-supported NiYSZ/8YSZ/LSCF solid oxide cell (active area of 2 cm^2, layers thickness 240/8/50 μm with respect to anode/electrolyte/cathode). The cell housing is made of Al2O3 and gas tightness is assured by a thin layer of Aremco Ceramabond 552. The SOFC housing is placed in a temperature-controlled furnace where temperature is measured by K-thermocouples. Bottled gases are used to supply the anode line with H_2, N_2, O_2, CO_2 and CH_4 while compressed air is sent to the cathode. The gas flowrates are regulated with Vögtlin Red-y digital mass flow meter controllers (accuracy: 0.2% on the full scale). A temperature-controlled water evaporator is used to add moisture to the anode feeding. All electric measurements are realized with an accuracy of 0.004% by a Keysight DAQ system.

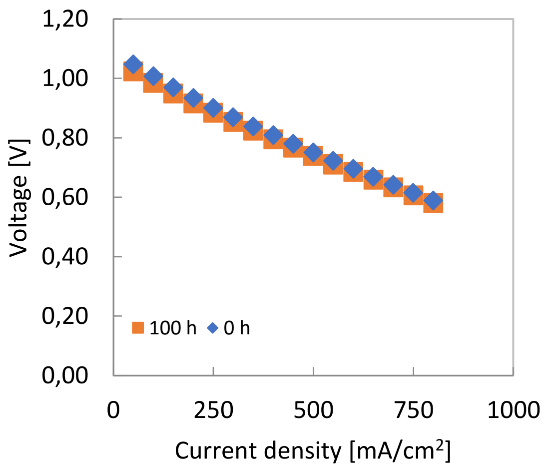
Results

From the literature survey, the test conditions were chosen. The cell is operated at 800°C, both to increase the membrane conductivity and reduce the risk of carbon deposition. The fuel electrode is supplied with simulated biogas and simulated air, achieving an Air/Biogas volume ratio of 0.4. Details about the test are resumed in Table 2.

Table 2 Test specifications.

T	Cathode		Anode						
	Total flow-rate [Sml/min]	Air	Total flow-rate [Sml/min]	Dry basis composition					H_2O
				Simulated biogas			Air		
				CH_4	CO_2	N_2	O_2	N_2	
800 °C	300	100%	50	46%	20%	6%	6%	23%	2.5%
800 °C	300	100%	50	55%	35%	7.5%	0%	0%	2.5%

The polarization curve of the SOFC (j-V curve) was recorded at the beginning of the cell exposure to simulated biogas+air and it is reported in Figure 1 (left). Cell voltage kept over 0.60 V until 750 mA/cm^2. After the polarization test, the cell was operated at constant load (1 A) for 100 hours. The cell voltage recorded during this part of the experiment was almost stable at 0.739 V a clear from Figure 1 (right). A new polarization curve was measured after the constant load test (Figure 1, left), showing that no sharp degradation occurred. Additional experimental results regarding the same type of cell fed with simulated biogas are referred to another work published by the authors [9]. Therefore, the measures collected were used to tune the model of this study.



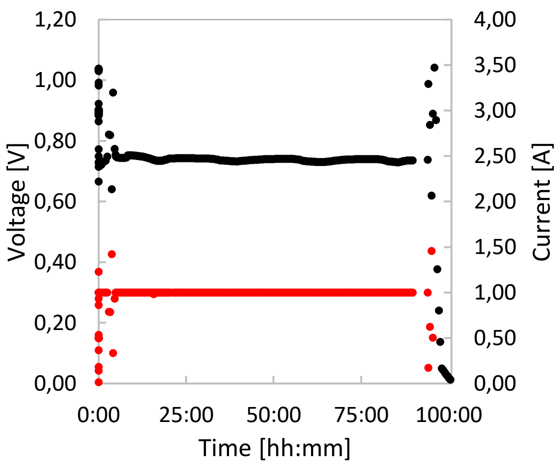


Figure 1 Experimental results: polarization curves at the beginning and end of exposure to simulated biogas+air (left), and constant load performance over 100 hours (right).

Model

Flowsheet description

The system model was developed in Aspen Plus simulator. The model flowsheet scheme is given in Figure 2. The system consists of two sections:

- External components: desulphurization filter, fuel/air pre-mixer, low temperature anode and cathode recovery heat exchanger, afterburner.
- SOFC: the thermochemical section (modelling equilibrium and redox reactions and internal heat management) is realized by Aspen Plus unit blocks, while the electrochemical section is based on a Fortran routine tuned on experimental data.

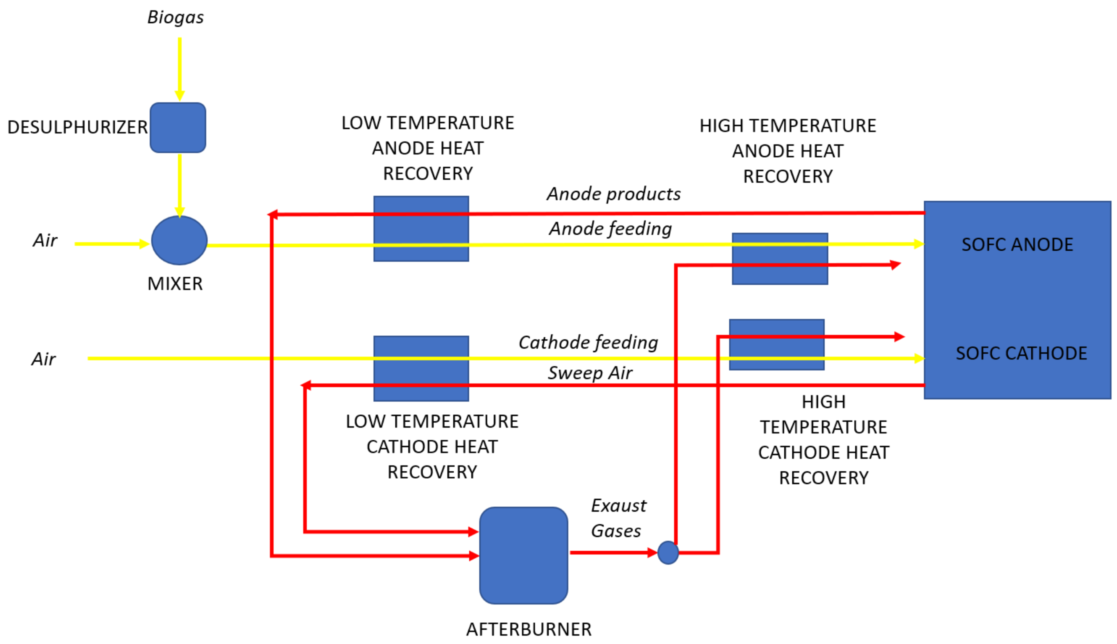


Figure 2 System Model: flowsheet

The simulation is run for the system fed with: 1) clean biogas, 2) clean biogas, plus air in a predefined molar ratio. All model inputs are resumed in Table 3.

Table 3 Model inputs.

Parameters	**Biogas**	**Biogas + Air**
Fuel flow rate	4.33 kg/h	
Fuel composition	CH_4 55%$_{vol}$, CO_2 35% $_{vol}$, N_2 7.5%$_{vol}$, H_2O 2.5%$_{vol}$	
Anode Air/biogas molar ratio	0	0.4
Cathode air flow rate	41.54 kg/h	
Voltage at 400 mA/cm^2	0.83 V	0.80 V
Temperature SOFC	800°C	
Gas Temperature at system inlet	25°C	
Gas Temperature at SOFC inlet	650°C	
Gas Temperature at system outlet	120°C	

Performance

Considering an efficiency of 95% at the inverter and 90% heat exchange efficiency for heat recovery in the system, the following results are issued from the model (Table 4). Keeping constant the biogas flowrate and calorific value, the introduction of a small amount of air in the anode feeding produce a reduction in both net electric power and thermal power. The first decreases from 10.58 kW to 9.42 kW, since: i) air increases polarization losses when the SOFC operated under load, ii) hydrogen partial pressure in the SOFC in lower, because air already promotes a partial oxidation of methane (reducing the hydrogen yield compared to reforming reactions). Thermal power decreases from 6.32 kW to 4.72 kW, because air preheating consumes internally part of the heat produced by the system. Nonetheless, this effect is mitigated by the exothermal behavior of internal fuel reactions. Both systems are environmentally friendly: NOx are practically absent in the exhaust gas stream; Sulphur is retained in the clean-up filter (this is mandatory for SOFC tolerance to Sulphur is 1 ppm) and net CO_2 emissions are zero considering the renewability of the fuel. However, due to the different electric efficiency, a power-specific CO_2 emission factor may be calculated: the system fed with biogas has a CO_2 usage factor of 606 g_{CO2}/kWh, while this indicator rises to 681 g_{CO2}/kWh in the configuration biogas+air.

Table 4 Simulation results

		Biogas	**Biogas+Air**
Power output	Electric power AC	10.58 kW	9.42 kW
	Thermal power	6.32 kW	4.72 kW
Efficiency	Electric efficiency AC	53.0%	47%
	Thermal efficiency	31.9%	23.9%
	Total energy utilization	85.3%	71.4%
	Specific fuel consumption	135 $g_{methane}$/kWh 409 g_{biogas}/kWh	151 $g_{methane}$/kWh 460 g_{biogas}/kWh
Emissions	CO_2 usage factor	606 g_{CO2}/kWh	681 g_{CO2}/kWh
	H_2S (filtered)	20 g/h	20 g/h
	NOx, SOx	Negligible	negligible

CONCLUSIONS

Simplified SOFC system based on direct feeding of fuel gases are attractive for micro and small-scale applications. However, in order to increase SOFC durability, air addition to the fuel is a promising strategy. As highlighted by the simulations, air addition to biogas leads to a decrease electric efficiency (47% vs. 53%), as well to a reduction of thermal efficiency (24% vs 32%). While air addition causes a decrease in performance, experimental evidence proves longer stability of performance. Further, the simulation will be extended to a significant time of operation, in order make a complete techno-economic study which considers efficiency as a function of time, implementing material degradation rates typical of each operating condition
(The complete multi-criteria analysis - including exergo-environmental aspects - is detailed in the full paper published elsewhere).

NOMENCLATURE

CHP	Combined Heat and Power generation
ICE	Internal Combustion Engine
NOx	Nitrogen Oxides
SOFC	Solid Oxide Fuel Cell
SOx	Sulphur Oxides

REFERENCES

[1] K. Hjort-gregersen, “Market overview micro scale digesters,” 2015.
[2] W. M. Budzianowski and K. Postawa, “Renewable energy from biogas with reduced carbon dioxide footprint: Implications of applying different plant configurations and operating pressures,” *Renew. Sustain. Energy Rev.*, 2015.
[3] S. A. Saadabadi, A. Thallam Thattai, L. Fan, R. E. F. Lindeboom, H. Spanjers, and P. V. Aravind, “Solid Oxide Fuel Cells fuelled with biogas: Potential and constraints,” *Renew. Energy*, vol. 134, pp. 194–214, Apr. 2019.
[4] A. Baldinelli, L. Barelli, and G. Bidini, “On the feasibility of on-farm biogas-to-electricity conversion: To what extent is solid oxide fuel cells durability a threat to break even the initial investment?,” *Int. J. Hydrogen Energy*, vol. 43, no. 35, pp. 16971–16985, 2018.
[5] Y. Shiratori, T. Ijichi, T. Oshima, and K. Sasaki, “Internal reforming SOFC running on biogas,” *Int. J. Hydrogen Energy*, vol. 35, no. 15, pp. 7905–7912, Aug. 2010.
[6] M. Pillai, Y. Lin, H. Zhu, R. J. Kee, and S. a. Barnett, “Stability and coking of direct-methane solid oxide fuel cells: Effect of CO2 and air additions,” *J. Power Sources*, vol. 195, no. 1, pp. 271–279, Jan. 2010.
[7] Y. Takahashi, Y. Shiratori, S. Furuta, and K. Sasaki, “Thermo-mechanical reliability and catalytic activity of Ni–Zirconia anode supports in internal reforming SOFC running on biogas,” *Solid State Ionics*, vol. 225, pp. 113–117, Oct. 2012.
[8] Z. Lyu, W. Shi, and M. Han, “Electrochemical characteristics and carbon tolerance of solid oxide fuel cells with direct internal dry reforming of methane,” *Appl. Energy*, 2018.
[9] A. Baldinelli *et al.*, “Quick Degradation Detection On Biogas-fuelled SOFCs,” *ECS Trans.*, vol. 91, no. 1, pp. 1571–1580, 2019.