

SOFC FUEL CELL TO BIOMASS GAS: THERMODYNAMIC MODELLING AND COMPARISON WITH GAS TURBINES

Alexandre Sordi

UNICAMP – University of Campinas – Mechanical Engineering School – Energy Department. P.O.Box 6039, ZIP CODE 13283970. University City – Campinas SP. email-asordi1@yahoo.unicamp.br

Ennio Peres da Silva

UNICAMP – University of Campinas – Physics Institute – Hydrogen Laboratory. P.O.Box 6039, ZIP CODE 13283970. University City – Campinas SP. email-lh2ennio@ifi.unicamp.br

Dmitri D. Lobkov

UNICAMP – University of Campinas – Mechanical Engineering School – Thermal and Fluids Department. P.O.Box 6039, ZIP CODE 13283970. University City – Campinas SP. email-lobkov@fem.unicamp.br

Daniel Gabriel Lopes

UNICAMP – University of Campinas – Physics Institute – Hydrogen Laboratory. P.O.Box 6039, ZIP CODE 13283970. University City – Campinas SP. email-danielg@fem.unicamp.br

Samuel N. M. de Souza

UNIOESTE – University of Parana State – Brazil. email-melegsouza@yahoo.com.br

Abstract. *The objective of this work is to model a fuel cell system of the type SOFC (Solid Oxide Fuel Cell) using biomass gas as fuel. This is a mixture of hydrogen (H_2), carbon monoxide (CO), methane (CH_4), hydrocarbons (C_xH_y), carbon dioxide (CO_2) and nitrogen (N_2). Electricity generation with biomass gas in a SOFC operating at temperatures from 800 to 1000°C is possible since the reforming of methane and carbon monoxide maximizes the molar fraction of hydrogen in the gas flow. The high temperature of a SOFC allows the internal reforming of biomass gas. The thermodynamic simulation of the reforming process and the production of electric work is done with objective of determining first and second law efficiency. The efficiencies of the SOFC system are compared to gas turbines in simple cycle, regenerative cycle and STIG. For the comparison, performances of gas turbines with power from 30 kW (micro-turbines) up to 30 MW were examined. Results show that a fuel cell is better for integration with atmospheric gasification reactors, and powers below 10 MW. On the other hand, gas turbines are better for integration with pressurized gasification and higher powers.*

Keywords: Fuel Cell, biomass gas, thermodynamics.

1. INTRODUCTION

The production of distributed electric energy (DG) consists of a source directly connected to the grid or to the consumer's meter. Having the production at the same location as the consumption is an advantage, as it avoids transmission losses. For DG to be competitive compared to centralized generation, conversion efficiency must be high. In this sense, the fuel cell is a promising technology.

The SOFC (Solid Oxide Fuel Cell) is a high-temperature fuel cell (800 to 1000°C). This operating feature is an advantage, as it does not require the use of pure hydrogen -- fuels such as natural gas, biogas, and biomass gasification gas (GGAS) can be used.

The present work develops a thermodynamic modelling of a system with a SOFC operating on GGAS. The exergetic efficiency of the SOFC is compared to that of existing gas turbines with powers between 30 kW and 30 MW.

2. SYSTEM SOFC / GGAS

Figure 1 illustrates the system for the production of electricity from the electrochemical conversion of GGAS in a SOFC. The GGAS exits the gasification reactor (Point 1) at 850°C. In the fuel cell, the reactions of GGAS internal reforming and the hydrogen electrochemical reaction take place. Air must be preheated to 500°C (Point 4); for this, part of the thermal energy of the hot exhaust gases of the SOFC (Point 5) can be used.

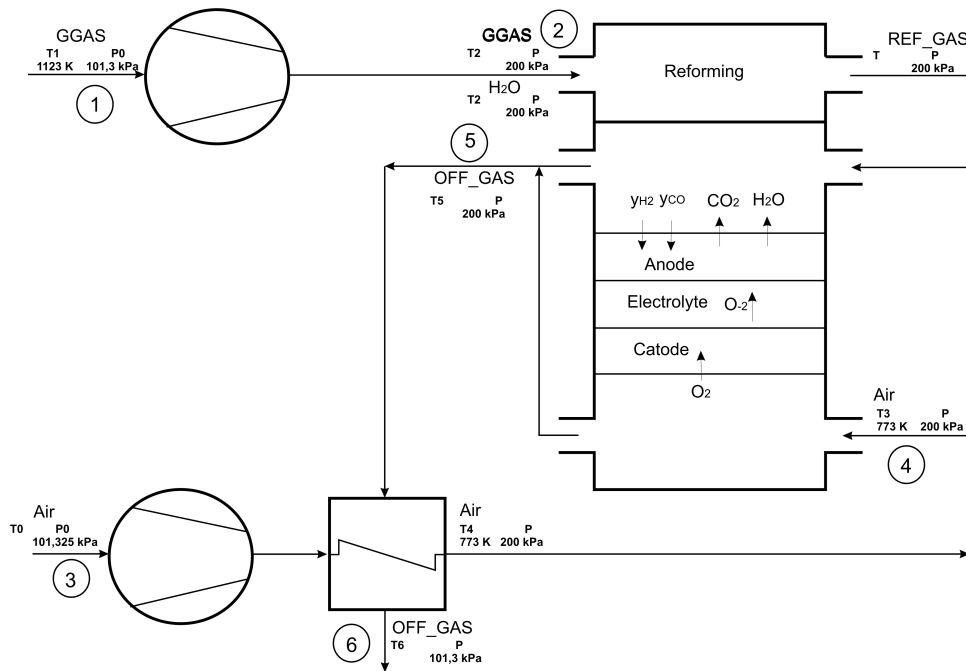
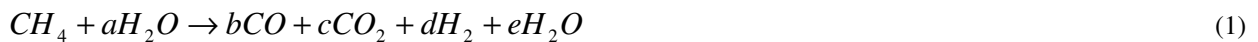


Figure 1. System SOFC / GGAS

3. THERMODYNAMIC MODELLING OF THE SOFC / GGAS SYSTEM

Since the SOFC operates at high temperature, it is possible to carry out the reforming of GGAS internally, i.e., there is no need of an external reforming reactor. For the GGAS composition, the reforming reactions are represented by the following equations according to SILVA (1989):



After the internal reforming of GGAS, the process of energy conversion in the fuel cell consists in the electrochemical reaction of hydrogen with oxygen producing steam, according to Eq.(4); part of the Gibbs free energy of this reaction is directly converted into electrical work.

According to Larminie & Dicks (2003), the thermodynamics of the fuel cell is represented by the equations below. Reaction of hydrogen with oxygen from air:



The First Law of Thermodynamics, neglecting the effects of kinetic and potential energy:

$$\delta Q - \delta W = dU \quad (5)$$

In a process under constant pressure, the relationship can be expressed as:

$$\delta Q - \delta W = dH - PdV \quad (6)$$

In the electrochemical reaction, work appears under two forms: electrical work to move electrons along an external circuit, and work due to gas expansion. Thus, Eq. (6) can be rewritten as:

$$\delta Q - (\delta W_{el} + PdV) = dH - PdV \quad (7)$$

The Second Law of Thermodynamics for a reversible process is:

$$\delta Q = TdS \quad (8)$$

Combination of Eqs. (6) and (7) results in the maximum electric work that can be produced by the fuel cell:

$$-\delta W_{el} = dH - TdS$$

Or:

$$-W_{el} = \Delta G = \Delta H - T\Delta S \quad (9)$$

Similarly, Eq. (9) on a molar basis is:

$$\Delta \bar{g}_f = \Delta \bar{h}_f - T \cdot \Delta \bar{s} \quad (10)$$

In the reaction described by Eq. (4) two electrons are transferred to a circuit external to the fuel cell. For each mol of hydrogen involved in the reaction, 2N electrons are transferred, where N is the Avogadro number. If -e is the charge of an electron, then the charge flow will be (DOE, 2002):

$$-2N \cdot e = -2F \quad (11)$$

where:

$$F = \text{Faraday constant } (9,649 \times 10^4 \text{ coulomb.mol}^{-1})$$

During the operation of the fuel cell, a difference of potential "E" appears between the cell electrodes. The electrical work is calculated by the equation:

$$w_{el} = -2F \cdot E \quad (12)$$

where:

$$w_{el} = \text{specific electrical work (J.mol}^{-1}\text{)}$$

$$E = \text{reversible potential (J.coulomb}^{-1}\text{)}$$

If there are no irreversibilities in the system, then the produced work will equal the Gibbs free energy of the reaction:

$$\Delta \bar{g}_f = -2F \cdot E$$

and

$$E = \frac{-\Delta \bar{g}_f}{2F} \quad (13)$$

Equation (13) calculates the ideal voltage or reversible potential for a fuel cell operating on hydrogen. For standard conditions (298.15 K and 101.325 kPa), the following holds:

$$E^0 = \frac{-\Delta \bar{g}_f^0}{2F} \quad (14)$$

Which results in 1.229 V for a fuel cell based in Eq. (1). However, in practice, the cell voltage is lower due to the overpotentials. These are known as: polarization by activation (α_{act}), ohmic polarization (α_{ohm}), and polarization by concentration (α_{conc}). Thus, the real operating voltage of a fuel cell is calculated by:

$$V = E - \alpha_{act} + \alpha_{ohm} + \alpha_{conc} \quad (15)$$

Thermodynamic analysis of the open system illustrated in Fig. 1 assumed the ideal gas model. Eqs. (16) and (17) represent enthalpy and entropy calculations for an ideal gas mixture.

$$\bar{h}_i = \sum_{i=1}^n y_i \cdot \left(\bar{h}_i^0 + \int_{T_0}^T \bar{c}_{p_i} \cdot dT \right) \quad (16)$$

$$\bar{s}_i = \sum_{i=1}^n y_i \cdot \left(\bar{s}_i^0 + \int_{T_0}^T \left(\frac{\bar{c}_{p_i}}{T} \right) \cdot dT - \bar{R} \cdot \ln(y_i) \right) \quad (17)$$

where:

\bar{h} = specific molar enthalpy (J.mol⁻¹)

\bar{s} = specific molar entropy (J.mol⁻¹.K⁻¹)

\bar{c}_p = specific molar heat (J.mol⁻¹.K⁻¹)

y_i = molar fraction (mol.mol⁻¹)

The mass balance and the energy balance are represented by Eqs. (18), (19) and (20).

$$\sum \dot{m}_{in} = \sum \dot{m}_{out} \quad (18)$$

$$\sum_{i=1}^n \dot{n}_i (\bar{h}_i(T))_P - \sum_{i=1}^n \dot{n}_i (\bar{h}_i(T))_R = 0 \quad (19)$$

$$\sum_{i=1}^n \dot{n}_{in} \cdot \bar{h}_{in} - \sum_{i=1}^n \dot{n}_{out} \cdot \bar{h}_{out} = \dot{Q} \quad (20)$$

where:

\dot{n} = molar flow (mol.s⁻¹)

\dot{m} = mass flow (kg.s⁻¹)

The first law efficiency of the SOFC / GGAS system is defined by:

$$\eta_I = \frac{\dot{W}_{el}}{\dot{n}(\text{LHV}(\text{GGAS}))} \quad (21)$$

The exergy balance for a control volume is:

$$\dot{W}_{VC} - \dot{I} = \dot{n}_{out} (\bar{ex}_{out}) - \dot{n}_{in} (\bar{ex}_{in}) \quad (22)$$

where:

\dot{I} = irreversibility rate (J.s⁻¹)

\bar{ex} = molar specific exergy (J.mol⁻¹)

LHV = lower heating value (J.mol⁻¹)

The definitions of physical and chemical specific exergy, according to Szargut et al. (1988) and Kotas (1995), are represented by Eqs.(23) and (24) respectively.

$$\bar{e}x_{ph} = (\bar{h} - \bar{h}_0) - T_0(\bar{s} - \bar{s}_0) \quad (23)$$

$$\bar{e}x_{ch} = \sum_{i=1}^n y_i \bar{e}x_{chi}^0 + \bar{R}T_0 \sum_{i=1}^n y_i \ln y_i \quad (24)$$

Where the total specific exergy is:

$$\bar{e}x = \bar{e}x_{ch} + \bar{e}x_{ph} \quad (25)$$

Physical and chemical exergies have been defined in relation to the reference environment proposed by Szargut et al. (1988). This source gives the standard temperature and pressure ($T_0 = 298.15$ K and $P_0 = 101,325$ kPa), as well as the composition of the standard atmosphere.

The exergetic efficiency of the SOFC / GGAS system was calculated considering as inputs the GGAS chemical exergy, the GGAS compression work, and the air compression for the fuel cell.

$$\eta_{II} = \frac{\dot{W}_{el}}{n(\bar{e}x_{CH}(GGAS)) + \dot{W}_{GGAS} + \dot{W}_{AIR}} \quad (26)$$

4. COMPARISON WITH GAS TURBINES

In order to compare the efficiencies of the SOFC / GGAS system and turbines, a survey of existing machines was done. Operation characteristics were found for industrial turbines, simple cycle aeroderivative turbines, and regenerative cycle micro and small gas turbines.

Table 1. Simple-cycle industrial gas turbines Machine Power.

Machine	ASE 8	ASE 40	ST 6	M1A 13A	M7A 01	GT 10	H 25
η_I	21.2	26.3	23.5	24.2	29.6	34.2	33.8
Power [kW]	506	3.000	646	1.490	5.530	24.630	27.500

Table 2 Simple-cycle aeroderivative gas turbines.

Machine	LM 2500 ⁺	LM 2500	LM 500	LM 1600
η_I	39	37	31	37
Power [kW]	30.200	25.000	4.500	15.000

Table 3 Regenerative-cycle gas turbines.

Machine	M 50	ST 5	C 60	C 30	T 100
η_I	38.5	32.7	28	25	30
Power [kW]	4.600	395	60	30	100

These operational characteristics of turbines refer to the lower calorific value of natural gas under ISO conditions. In order to use GGAS of low ($4.500 - 5.500$ kJ.m⁻³) and medium ($9.000 - 13.000$ kJ.m⁻³) calorific value (COHEN et al., 1996), the turbine must be designed to operate with a higher gas flow volume.

5. RESULTS

Figure 2 illustrates the polarization curve of the SOFC cell at 800°C. Operation voltage of each cell in the stack varies under real conditions from 0.6 to 0.8 volts. Taking into account the polarization curve, a tension of 0.76 V corresponds to a current density of 700 mA.cm⁻²; this is the nominal condition of the SOFC, which was considered in the electricity production calculations.

Figure 3 illustrates the first and second law efficiency variations as a function of the methane molar fraction in GGAS composition. The lower limit of this molar fraction corresponds to a gaseous mixture produced by gasification with air, and the upper limit to a gaseous mixture produced by gasification with indirect heating and steam injection. A tendency to a reduction in the first law efficiency with increasing methane molar fraction is observed, because the variation in the energy ratio due to the calorific value of the gaseous mixture is higher than the produced electric energy.

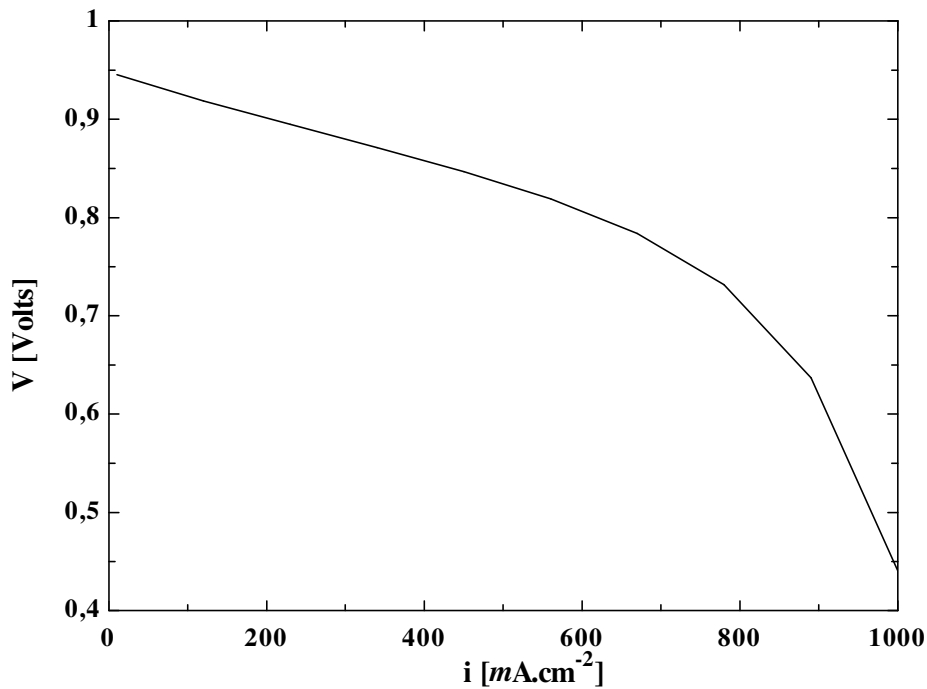


Figure 2. SOFC cell polarization curve at 800°C

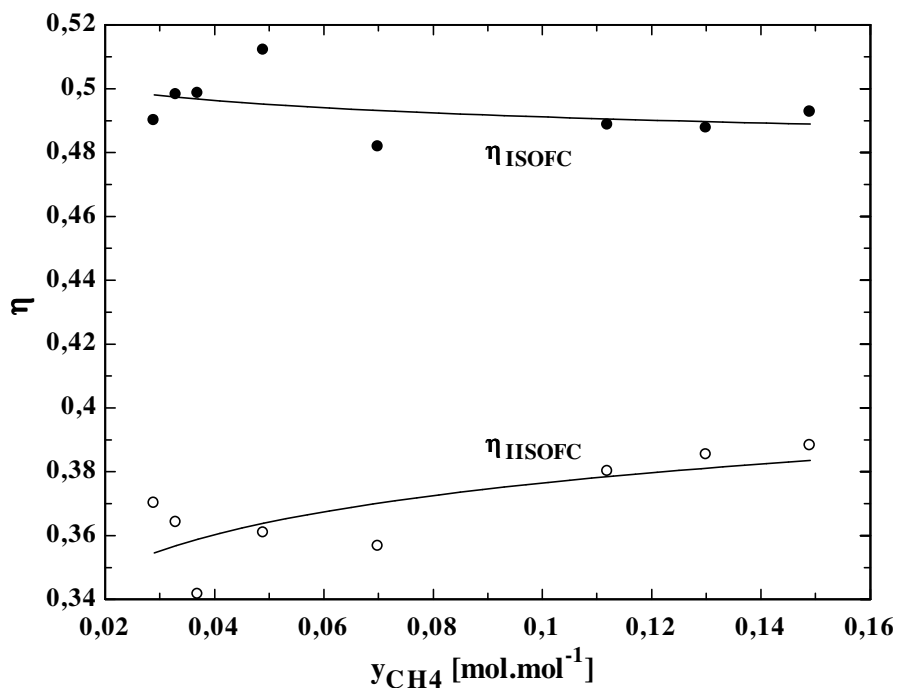


Figure 3. Efficiencies of the SOFC/GGAS system as a function of y_{CH_4}

However, the first law efficiency is not a good parameter to measure system performance, because it is not indicative of the quality, and hence of the potential of the mixture for the production of hydrogen and electricity. On the other hand, the second law efficiency, which displays a clear tendency to increase with the methane molar fraction, does indicate the potential of the gaseous mixture for the production of hydrogen and electricity.

The deviation of some points from the curves in the graph of Fig. 3 is due to the fact that the hydrogen available to the fuel cell depends also on the steam reforming of other species such as CO and C_nH_m , as well as on the hydrogen molar fraction in the GGAS itself. Figure 4 shows the variation in system efficiency as a function of the hydrogen molar fraction in GGAS composition.

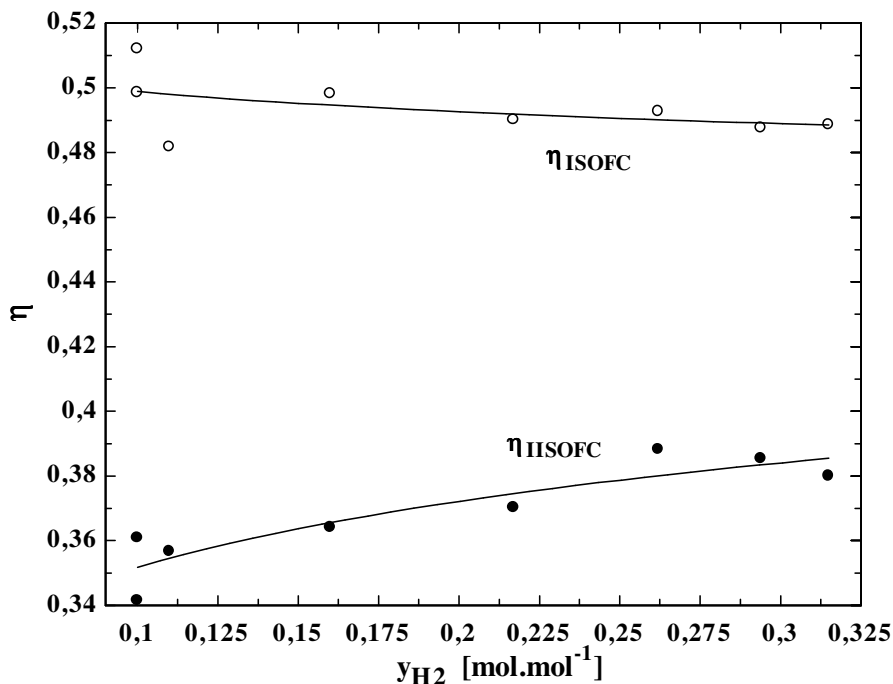


Figure 4. Efficiencies of the SOFC/GGAS system as a function of y_{H_2}

For the SOFC/GGAS system the highest exergetic efficiency is reached for the gaseous mixture produced by gasification with indirect heating, which has the highest hydrogen production for a given gas flow. However, the construction of a pilot plant should foresee the production of steam for the gasification reactor; in the case of a SOFC it is possible to use the thermal energy of exhaust gases to produce steam for the system.

It is important to mention that the gasification processes can be of atmospheric or high pressure. According to DOE (2002) and Larminie & Dicks (2003), with a higher operation pressure there is an increase in fuel cell tension and efficiency. Figure 5 shows tension variation as a function of fuel cell operation pressure. The upper pressure limit in Figure 5 can occur in some gasification processes, but not in fuel cells. A substantial pressure increase in the fuel cell would not be justified because of the extra energy spend in its pressurization.

Thus, SOFC / GGAS integration should be done for gasification processes under atmospheric pressure. Integration of a SOFC with a pressurized gasification reactor can be viable if the SOFC exhaust gas is directed to a gas turbine (hybrid system). The latter can produce power to drive the air compressor, and the remainder can be used to produce electric energy. Hybrid systems using natural gas as fuel are currently under test.

Hybrid systems are promising for distributed electric generation, since they can attain an electrical efficiency as high as 0.75 even in a small scale. However, they still face several technical problems related to the integration of an electrochemical device to a thermal machine.

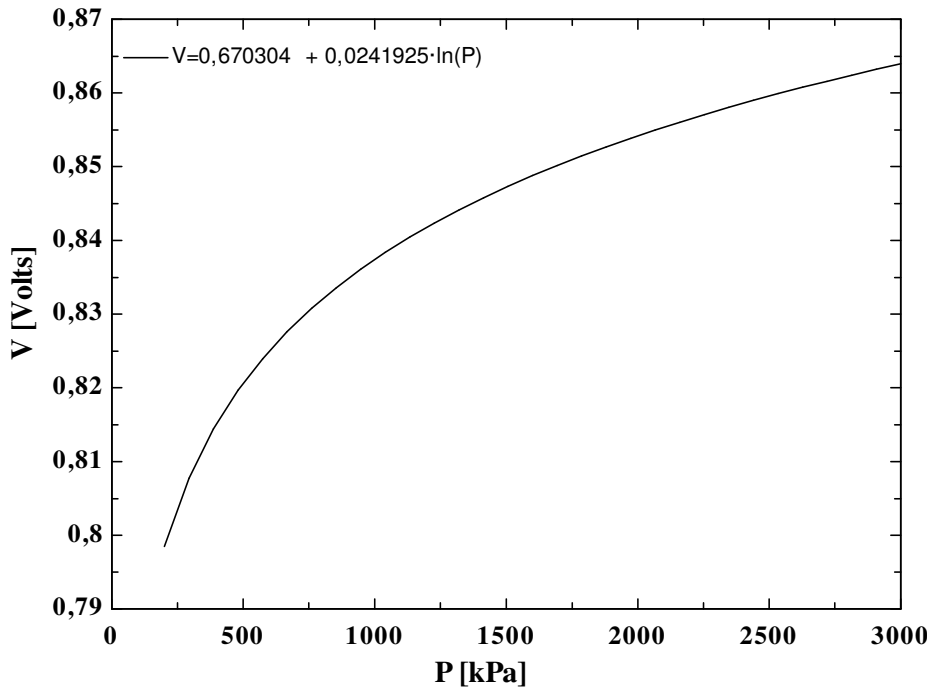


Figure 5. SOFC voltage variation as a function of pressure

In order to compare the exergetic efficiencies of the SOFC system and a system with gas turbine, the graphs below illustrate the efficiency variation of both technologies as a function of power. Figure 6 shows the variation of exergetic efficiencies of SOFC and gas turbines in a simple cycle for the process of gasification with steam injection, indirect heating, and under atmospheric pressure. This is not the best condition for gas turbines due to the consumption of energy to compress the gas up to the operation pressure at the combustion chamber; in this case the exergetic efficiency of the SOFC system is always higher in that power range. The same happens in the comparison to regenerative cycle turbines (Fig. 7): these machines are smaller, since the regenerative cycle is only advantageous for low pressure ratios.

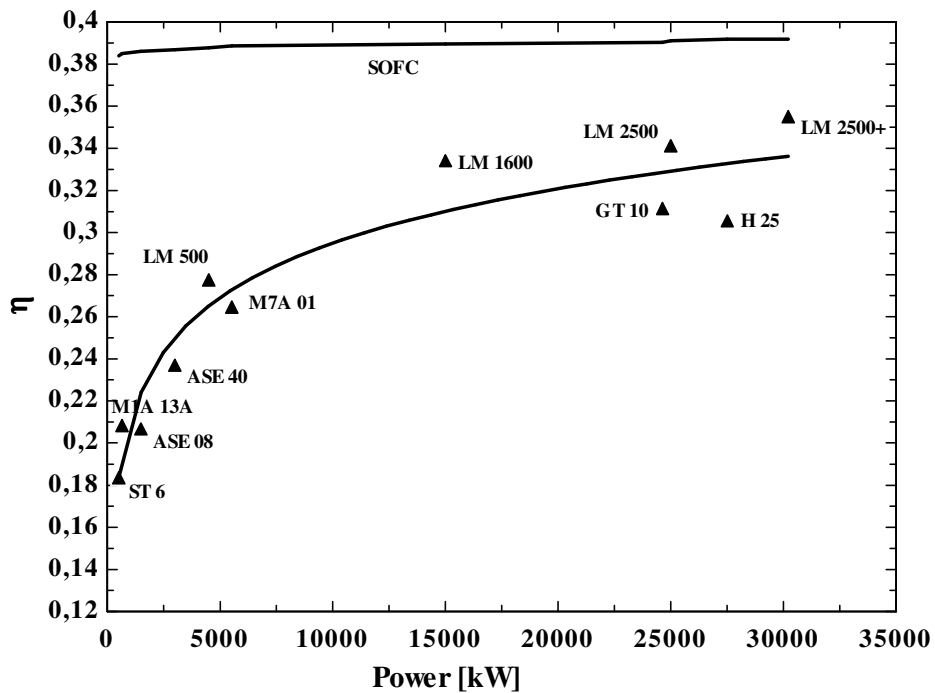


Figure 6. Efficiency comparison between simple cycle gas turbine and SOFC

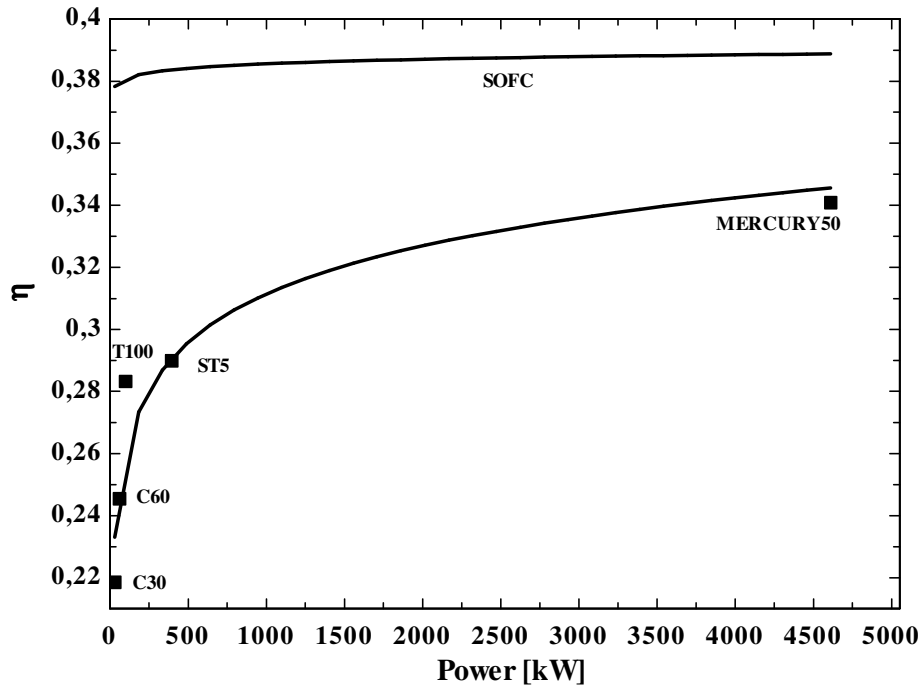


Figure 7. Efficiency comparison between regenerative cycle gas turbine and SOFC

On the other hand, integration of a gas turbine to a pressurized gasification system in which part of the air is extracted from the compressor and directed to the gasification reactor results in an increase in efficiency. Furthermore, the turbine exhaust heat is used for the production of steam, and if this is injected in the combustion chamber or in the expander itself, an increase of up to 30% of the produced power can be achieved, increasing the system efficiency. The steam injection process is also called STIG cycle (steam injected gas turbine), and is of course limited to a certain permissible maximum, in order to avoid an adverse effect on combustion stability. Figure 8 shows the efficiency comparison between STIG cycle aeroderivative turbines and SOFC. It can be seen that SOFC displays a higher efficiency between 5 and 10 MW, and loses its advantage beyond these powers.

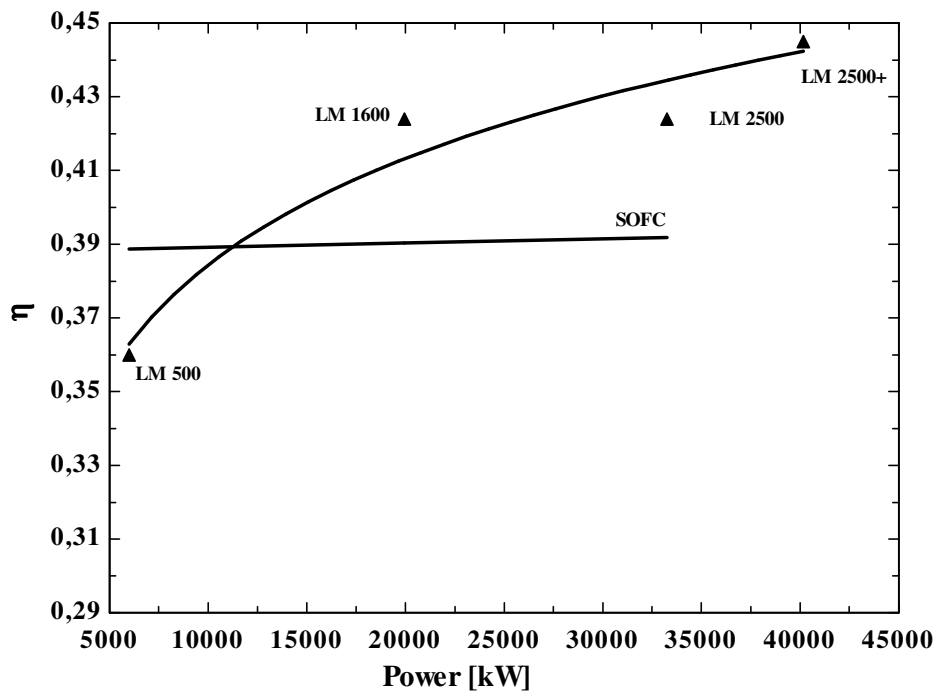


Figure 8. Efficiency comparison between STIG cycle gas turbine and SOFC

6. CONCLUSION

The exergetic efficiency of the SOFC/GGAS system varies with the composition of the gaseous mixture. The highest efficiency -- around 0.39 -- is reached for gas mixtures produced by gasification processes with indirect heating and steam injection, against 0.35 for an air gasification system. A fuel cell system is more appropriate for integration with gasification reactors operating at atmospheric pressure, since a SOFC efficiency increase through pressure increase is not justified because of the energy expended for pressurization.

In terms of exergetic efficiency, the SOFC system is superior to gas turbine systems with both simple and regenerative cycles with atmospheric gasification. However, turbines above 10 MW operating in a STIG cycle with pressurized gasification are more efficient.

Thus, if steam injection into turbines is viable, and if combustion stability can be assured, then, in terms of exergetic efficiency, the SOFC fuel cell is superior to turbines for powers under 10 MW.

7. ACKNOWLEDGEMENTS

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