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Biomass integrated gasifier-fuel cells: Experimental investigation on wood syngas tars impact on NiYSZ-anode Solid Oxide Fuel Cells

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ABSTRACT

The aim of this work is to assess the feasibility of a Biomass Integrated Gasifier Fuel Cell (B-IGFC) plant. High temperature Solid Oxide Fuel Cells (SOFC) are the most efficient energy systems currently being developed and they show good fuel flexibility thanks to their high operational temperature. For the application here discussed, the fuel major active species are H_2, CO and CH_4; yet, in wood-derived syngas small amounts of higher hydrocarbons are produced too. Among them, tars are claimed to be biomass Achille's heel, causing severe issues in internal combustion engines and turbines. Conversely, SOFCs might be able to decompose tars with a gain on cell performance. However, in order to avoid fast degradation, tars concentrations have to be below a critical threshold. In this work, SOFC operation with real wood syngas from a pilot batch gasifier is firstly demonstrated. Then, longer tests are repeated under controlled conditions, artificially reproducing wood syngas with and without tars. Tests demonstrated that commercial NiYSZ-anode cells are able to work on syngas with a model tar (toluene) concentration up to 10 g/N m^3, exhibiting a voltage gain with regard to performances on syngas without model tar. No material degradation was observed after the experiments. As a final result, this paper aims at providing a proof of concept of a simplified B-IGFC system design, in order to reach its cost-effectiveness on small-scale installations.

1. Introduction

Climate change and resources exploitation have become one of the hardest challenges humanity is facing. COP21 recently stressed the importance of energy saving, clean and efficient energy generation and fuel supply diversification. In this scenario, renewable energy resources (RES) are a promising alternative to traditional fuels and, among them, a key-role is played by biomass [1], which are spread all over the world. In addition to that, biomass allows an easier energy storage, so that power production can be scheduled according to power demand thus overcoming the issue of availability which is the main drawback of other RES, such as solar and wind.

Solid Oxide Fuel Cells (SOFCs) are one of the most efficient energy systems and they are able to work with a wide variety of fuels. As reported in [2–4], SOFCs are good candidates for the realization of efficient integrated systems. In particular, SOFCs can run on wood-derived synthetic gas, a mixture containing hydrogen, carbon monoxide, carbon dioxide, methane, nitrogen and other minor species [5,6]. Feedstock heterogeneity and gasification process parameters (e.g. gasification agents [7]) variability might influence SOFCs performances. However, modelling studies on the utilization of bio-derived fuels in SOFC devices predicted an efficiency up to 50% based on biomass lower heating value [8–11]. Such interesting figures call for an experimental validation.

System modelling studies usually do not take into account syngas minor components influence on SOFC performance. In a real system operation, despite very low concentration, they can have a heavy impact. In particular, regarding biomass gasification syngas minor components, tars are of primary concern. They include many organic compounds (phenols, 1-ring aromatics, PAHs) with a high boiling temperature. In conventional systems, they are claimed to be responsible of equipment failure: in [12,13], it is reported that ICEs and GTs tolerance limits are 50–100 mg/N m^3 and 5 mg/N m^3 respectively. Conversely, SOFC tolerance is

Abbreviations: B-IGFC, Biomass Integrated Gasifier Fuel Cell; BC, button cell; DAQ, Digital Acquisition System; FMC, flow meter controllers; GC, gas chromatograph; GT, Gas Turbine; ICE, internal combustion engine; NiYSZ, Nickel Yttria-Stabilized-Zirconia; NiGDC, Nickel Gadolinia-doped-Ceria; PAHs, Polycyclic Aromatic Hydrocarbons; PS, Power Supply; R, electronic load; RES, Renewable Energy Sources; SOFC, Solid Oxide Fuel Cells; TR, thermocouple.
Subscripts: db, dry basis; wb, wet basis.

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Nomenclature

A	SOFC active area, [cm^2]	n_{ij}	Partial flow rate of species *i* in stream *j*
F	Faraday constant, 96485 C/mol	p_{0i}	Saturation pressure of species *i*, [kPa]
j	Current density, [mA/cm^2]	p_{0tot}	Total pressure, [kPa]
i	Current, [A]	**T**	Temperature, [°C],[K]
LHV	Low heating value, [kJ/Nl],[kJ/mol]	**V**	Voltage, [V]
n_{eq}	Equivalent fuel flow rate, [mol/s],[ml/min]	x_{ij}	Molar fraction of species *i*, in stream *j* [%]

expected to be higher, thanks to high operational temperature and catalysts (e.g. Nickel) enabling tar decomposition. Therefore, it is challenging to investigate whether SOFC tolerance to tars is within typical wood syngas tar loads, in order to achieve SOFCs bio-syngas feeding without meeting with quick degradation issues [14–16]. As a consequence, wood syngas featuring a small tar concentration might not require a dedicated cleaning unit interposed between the gasifier and the end-user device (SOFC). This is a key-point, especially in the outlook of small-scale distributed applications that call for complexity and capital expenditure reduction to achieve techno-economic feasibility [17].

In the literature, just few experimental works deal with the coupling of gasification and SOFCs. In particular, [18–20] evaluated SOFC operation with commercial gasifiers equipped with robust cleaning units. In those works, the most used gasification technology is the fluidized bed, which is typically suitable for application in the power range of 100 kW. Conversely, Biomass Integrated Gasifier Fuel Cell (B-IGFC) low-capacity applications are far more affordable in the outlook of distributed power generation systems. In this frame, fixed bed gasifiers seem to be the most promising choice.

According to the specific fixed bed inner design and process conditions, syngas components percentages and tars content are variable. Among fixed bed configurations, downdraft fixed bed gasifiers syngas output features good properties for the utilization in a SOFC [21], such as a low tar content: literature reports that the expected tar concentration for downdraft syngas is less than 1 g/N m^3 [22,23]. More recent experimental works confirmed that, after condensing low boiling-point components, tar residue was measured to be in the neighbourhood of 1 g/N m^3. Other authors [16] measured a larger tar concentration on wood syngas, albeit smaller than 10 g/N m^3. Low tar load is due to the temperature profile inside the reactor: temperature higher than 800 °C enables primary and secondary pyrolysis products decomposition into tertiary tars (alkyl-aromatics, PAHs) [22]. Because of that, downdraft tars are mainly aromatic hydrocarbons, such as those shown in Table 1. Table 2 displays typical wood syngas bulk compositions achieved when air is used as oxidizing medium.

SOFC tolerance to tars was investigated in a few studies, usually reproducing fuel mixtures with technical gases. Most scientific works assess SOFC behaviour with a simulated syngas enriched with a single tar compound (or at most a blend of few compounds), referred as model tar. The authors of [29] investigated tar impact on NiYSZ-anode SOFC performances using both 1-ring aromatics (toluene and benzene) and a mixture of several compounds. They found out that 1-ring aromatic model tar caused a higher polarization resistance, because of their propensity towards catalytic breakdown into carbon. With similar results, in [30] a comparison between real tar and 1-ring model tar (toluene) impact on different SOFC anode materials was accomplished. Furthermore, in [31,33], other tests with benzene model tar were carried out, exposing a NiGDC-anode cell to hydrogen plus 15 g/N m^3 benzene. Although they did not observe overpotential changes, post-experimental SEM showed large carbon deposits on the anode surface. For these reasons, they claim that a longer exposure to such benzene concentrations, in a hydrogen matrix, could lower cell performance. Then, using a simulated syngas as fuel with 5 g/N m^3 benzene concentration, they measured higher overpotential but no carbon deposition. Despite coking issues, model tar addition results in increasing cell open circuit voltage as a consequence of model tar decomposition, as demonstrated by [33,34] (model tar naphthalene) and by [35,36] (model tar toluene, NiGDC-anode cells). SOFC stable operation under toluene-laden syngas was demonstrated in [37], up to 20 g/N m^3 toluene concentration in a syngas matrix made of 16% H_2, 16% CO_2 and 7.6% CH_4. On the contrary, when tar content exceeds SOFC tolerance threshold, it causes cell performances loss and material degradation, mainly because of carbon deposition and catalyst deterioration [38–40].

Hence, with regard to the state of the art, this paper aims at producing advances in the integration of SOFCs with a gasification facility. In particular, the application of small-scale downdraft gasifiers equipped with a simplified cleaning unit is discussed and experimentally tested. In this outlook, it is important to define a good management of the gasification process so that wood syngas bulk composition is compatible with a long-lasting SOFC operation. In this framework, current literature reports experiments performed on simulated fuel mixture which are not consistent with a real gasification process. Thus, the main target is to provide an experimental proof of concept that makes modelling projections easily available in the scientific literature more interesting. For what concerns SOFC technology, to provide results that are relevant for a pilot or demonstration installation, commercial NiYSZ-anode SOFCs are employed. NiYSZ is the material which is more mature from a manufacturing point of view, although it is not optimized for the operation under tar-laden fuels.

Table 1
Average composition of the tar fraction in wood syngas produced by downdraft gasifiers, as reported into other researches [24].

Tar compound	Percentage (%)
Toluene	28
Naphthalene	18
Styrene	9
Indene	9
Phenol	7
Others	29

2. Experimental activity

Experimental results presented in this work are meant to demonstrate the feasibility of the B-IGFC concept, with a specific focus on SOFC tar tolerance. To accomplish this, at first SOFC is fed directly with clean real wood syngas; then, wood syngas is artificially reproduced with technical gases, both neglecting and considering tars, so that a longer test is performed with SOFC. Tests with simulated wood syngas are useful to verify SOFC material