PROCEEDINGS OF ECOS 2023 - THE 36TH INTERNATIONAL CONFERENCE ON
EFFICIENCY, COST, OPTIMIZATION, SIMULATION AND ENVIRONMENTAL IMPACT OF ENERGY SYSTEMS
25-30 JUNE, 2023, LAS PALMAS DE GRAN CANARIA, SPAIN

Pollutant testing (NOx, SO_2 and CO) of commercialized micro-combined heat and power (mCHP) fuel cells

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Abstract:

Energy transition currently brings focus on fuel cell micro-combined heat and power (mCHP) systems for residential uses. The two main technologies already commercialized are the Proton Exchange Membrane Fuel Cells (PEMFCs) and Solid Oxide Fuel Cells (SOFCs). The pollutant emissions of one system of each technology have been tested with a portable probe both in laboratory and field-test configurations. In this paper, the nitrogen oxides (NOx), sulphur dioxide (SO_2) and carbon monoxide (CO) emission levels are compared to other combustion technologies such as a recent Euro 6 diesel automotive vehicle and a classical gas condensing boiler. At last, a method of converting the concentration of pollutants (in ppm) measured by the sensors into pollutant intensity per unit of energy (in mg/kWh) is documented and reported. This allows for comparing the pollutant emissions levels with relevant literature, especially other studies conducted with other measuring sensors.

Both tested residential fuel cell technologies fed by natural gas can be considered clean in terms of SO_2 and NOx emissions. The CO emissions can be considered quite low for the tested SOFC and even nil for the tested PEMFC. The biggest issue of natural gas fuel cell technologies still lies in the carbon dioxide (CO_2) emissions associated with the fossil fuel they consume.

Keywords:

SO_2; Fuel cell; mCHP, NOx, pollutant emissions; CO.

1. Introduction

In its latest Sixth Assessment Report in April 2022, the Intergovernmental Panel on Climate Change has reported a maximum carbon budget of 890 $GtCO_2$ that humanity can emit from January 1st 2020 in order for global warming to likely remain under the +2 °C widely acknowledged limit compared to preindustrial temperature levels [1]. Even at residential scales, this much-needed GreenHouse Gases (GHG) mitigation brings focus on cleaner power sources and on combined heat and power (CHP) systems, such as fuel cells [2]. The two primary technologies that have already been commercialized are the Proton Exchange Membrane Fuel Cells (PEMFCs) and the Solid Oxide Fuel Cells (SOFCs), which are compared in Table 1. GHG emissions (in terms of CO_2 or CO_{2eq}) of such systems have already been addressed [3, 4] but another key element in assessing the environmental impacts of those technologies lies in the other common air pollutants : the emissions of nitrogen oxides (NOx), sulphur dioxide (SO_2), and carbon monoxide (CO).

The novelty of this study lies within the evaluation of SO_2, NOx and CO emissions of fuel cell technologies commercialized for residential applications in both laboratory and field-test configurations (in real dwellings in Belgium). This has been performed on several machines of different ages, for one PEMFC-based and one SOFC-based technology, thanks to a combustion analyser portable meter. This study compares the emission levels of those pollutants measured for the studied fuel cell systems with other combustion technologies, such as a recent Euro 6 diesel automotive vehicle and classical gas condensing boilers. To facilitate comparison with relevant literature, a method of converting the concentration of pollutants (measured in ppm) detected by the sensors into pollutant intensity per unit of energy (in g/kWh) has been documented and reported, which has never been the case in an academic paper to the knowledge of the authors. This approach enables the assessment of pollutant

https://doi.org/10.52202/069564-0104

emissions levels across different studies, including those conducted using alternative measuring sensors.

Table 1. Comparison between PEMFCs and SOFCs. Reproduced and adapted from reference [10].

Fuel cell type & Charge carrier	Typical electrolyte	Major contaminants	Stack operating temperature (°C)	Specific advantages	Specific disadvantages	LHV Electrical efficiency (%)
PEMFC & H+	Solid Nafion®, a polymer	Carbon monoxide (CO) [a] Hydrogen sulfide (H_2S) [a]	60–80 (only low-temperature PEMFC are currently commercialized [5])	Highly modular for most applications High power density Compact structure Rapid start-up due to low temperature operation Excellent dynamic response	Complex water and thermal management [a] Low-grade heat High sensitivity to contaminants [d] Expensive catalyst Expensive Nafion® membrane [6]	40-60 (with H_2) (Currently limited to 38.5 with CH_4 as some fuel needs to be burned to provide heat to a methane reformer [7])
SOFC & O^{2-}	Solid yttria-stabilized zirconia, i.e. YSZ, a ceramic	Sulfides	800-1000	High electrical efficiencies High-grade heat High tolerance to contaminants Possibility of internal reforming Fuel flexibility Inexpensive catalyst Simpler water management (SOFC can work at a perfect drying state [8])	Slow start-up Low power density Strict material requirements High thermal stresses Sealing issues Durability issues High manufacturing costs	55-65 (with H_2) (Currently limited to 60%-65% with CH_4 [5, 9], i.e. still high thanks to the SOFC fuel flexibility)

[a] Contaminants, thermal and water management of PEMFC stacks have been discussed more deeply in another work [11].

2. Material and methods

2.1 Tested systems

2.1.1 PEMFC hybridized to a gas condensing boiler

The PEMFC is not a standalone unit. It is hybridized to a gas condensing boiler and to a Domestic Hot Water (DHW) tank. It is fed by natural gas and is designed to cover all the heat demands, including DHW, of residential houses and to participate locally in the electrical production. This particular system exists in several versions all based upon the same PEMFC module of nominal constant power of $0.75kW_{el}$ (and $1.1kW_{th}$) and the same 220L DHW tank. The only module that may vary is the gas boiler that is supposed to ensure peak heat demands. Indeed, it exists in four rated power versions from 11.4 to $30.8kW_{th}$, depending on thermal needs [12]. The heat rate output of the field-test system considered in this study is rated to 24.5 kW_{th} and is located in Huy, in Belgium. System's architecture is presented in Figure 1, which does not show the double walled chimney used for both the air inlet and flue gases exhaust [13]. Main datasheet characteristics are presented in Table 2.

Table 2. PEMFC gas boiler hybrid expected targets (data published by manufacturer) [12].

Datasheet figures	Values
Maximum electrical production a year	$6200kWh_{el}$
Fuel cell rated electrical and thermal power as defined by EN 50465 [2]	$0.75kW_{el}$ & $1.1kW_{th}$
Electrical fuel cell efficiency	37% (LHV)
Max global Fuel cell efficiency	92% (LHV)
Max boiler efficiency (at rated power) [a]	108.6% (LHV)
NOx, class 6 [14]	7.2 mg/kWh
Size without chimney (Hight x Width x Depth)	1800 mm x 595 mm x 600 mm

[a] Considering High Heating Value (HHV) to Low Heating Value (LHV) ratio of 1.1085 [15]

The complete system behaviour is heat driven. Its PEMFC has not been designed to be driven by the electrical demand and it is preferable that it runs as long as possible. It includes a methane reforming

 https://doi.org/10.52202/069564-0104

apparatus to feed the fuel cell stack with clean hydrogen and requires an automated fuel cell shutdown recovery procedure of 2.5 hours at least every two days to handle some reversible ageing processes [11]. For further information, this system has been quite exhaustively studied in other publications [2, 4, 11, 16, 17, 18].

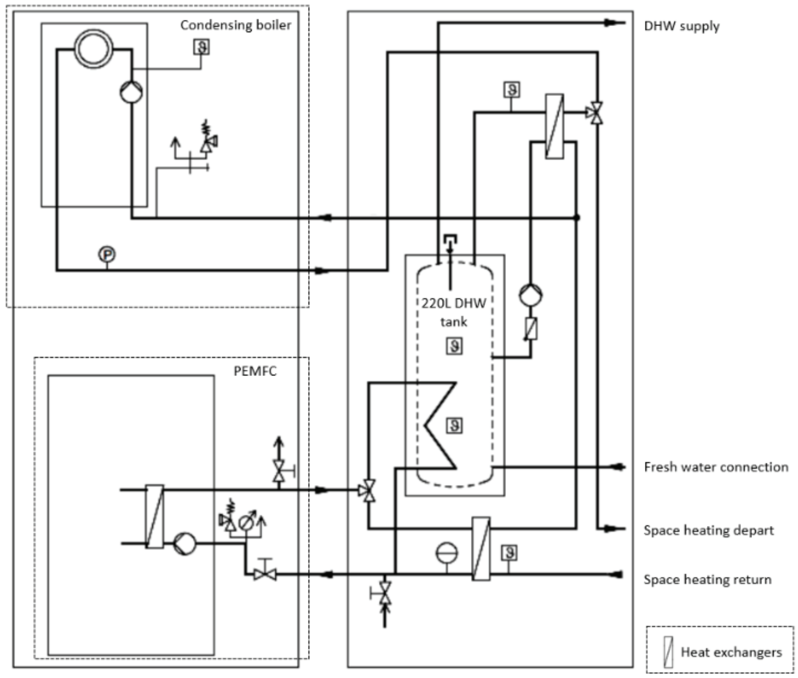

Figure 1. PEMFC system's architecture, including two heat exchangers, several 3-way valves, several circulators, the gas condensing boiler and the DHW tank [4].

2.1.2 SOFC

The studied SOFC is also fed by natural gas. It is designed to provide 1.5 kW_{el} of nominal output power with a high announced LHV electrical efficiency of 60%, along with a heat recovery of 0.6 kW_{th} representing a LHV thermal efficiency up to 25% [3]. The output power can be modulated down remotely (by the manufacturer, upon the owner's request) as wanted in the 0.5 - 1.5 W_{el} range, affecting those announced efficiencies. It is not advised to completely shut it down because thermal cycles affect its durability and because start-up operations are long and have been reported in the user manual to last up to 30 hours [19] .

Discarding its chimney, the system has approximately the same size as a dishwasher, as it can be seen in Figure 2. Its internal schematics has not been disclosed but has been discussed in a previous publication [3], based on observations of the system and cogeneration SOFC literature. Amongst other particularities, the reforming process of the inlet natural gas (into hydrogen) is not only internal, i.e. directly at the anode onto the stack (allowed with high operating temperatures occurring with that fuel cell technology [20]), but it also uses an external steam reformer upstream of the stack (called 'pre-former' [3]). For information, the newer version of this system is stated by the manufacturer as belonging to class 6 in terms of NOx [21] (according to EN 15502-1 [14]) but the exact emission levels have not been reported, to the knowledge of the author.

Figure 2. Tested mCHP SOFC in the laboratory facilities of the University of Liege [22].

2.1.3 Gas condensing boiler

The tested mural gas condensing boiler dates from 2005 and is quite classical. Its identification name is 'Buderus Logamax plus GB142-45' and it can provide up to 45 kW_{th} (that can be modulated down to 30%). It is able to provide heat to an optional DHW tank but cannot provide instantaneous DHW directly as it has only one hydraulic inlet and one hydraulic outlet (used in close circuit configurations). The emissions of CO and NOx are reported by the manufacturer respectively to 15 mg/kWh and 20 mg/kWh [23].

2.1.4 Euro 6 diesel vehicle

The tested vehicle is a 4-year BMW X1 sDrive18d that is proper maintenance and had 111210 kilometers on the odometer at the moment of the test. Its four-stroke engine has four cylinders and represents a displacement of 1995cm³. Net power is 100 kW at 4000 rpm. The certificate of conformity presents average emissions on the New European Driving Cycle (NEDC) for CO and NOx respectively of 86.8 mg/km and 19.2 mg/km. Maximum Real Driving Emissions (RDE) NOx emissions are reported to be equal to 168 mg/km. Considering an effective consumption of 6L per 100 km (according to the dashboard of the vehicle), considering a diesel LHV of 43.51 MJ/kg and a density of 827 kg/m³ [24], those emissions correspond respectively to 145 mg/kWh (average CO emissions on the NEDC), 32 mg/kWh (average NOx emissions on the NEDC) and 280 mg/kWh (maximum Real Driving Emissions NOx). They are relative to the diesel LHV input to the engine.

2.2 Measurement device

To perform the pollutants emissions analyses of the tested systems, the same portable combustion analyser meter has been used. It is called 'Multilyzer STx' and is shown in Figure 3 whereas its specifications are shown in Table 3.

It measures CO, NO, NO_2 and SO_2 in ppm, whereas O_2 and CO_2 concentration levels are expressed in percentage (by volume). Carbon monoxide sensors have generally a significant cross-sensitivity to hydrogen, meaning that the real carbon monoxide concentration can be overestimated if hydrogen is present as well in the tested gas sample [25]. Therefore, as presented in Table 3, the 'Multilyzer STx' combustion analyser portable meter has implemented a hydrogen compensation for its carbon monoxide measurements.

https://doi.org/10.52202/069564-0104

Figure 3. 'Multilyzer STx' combustion analyser portable meter.

Table 3. Specifications of the 'Multilyzer STx' combustion analyser portable meter [26].

Sensor	Range	Accuracy	Resolution
NO	0 - 5000 ppm	± 5 ppm (< 50 ppm) ± 5% reading (> 50 ppm)	1 ppm
NO_2	0 - 500 ppm	± 10 ppm (< 50 ppm) ± 10% reading (> 50 ppm)	1 ppm
SO_2	0 - 5000 ppm	± 10 ppm (< 200 ppm) ± 5% reading (> 200 ppm)	1 ppm
CO (hydrogen compensated)	0 - 10000 ppm	± 5 ppm (< 50 ppm) ± 5% reading (> 50 ppm)	1 ppm
O_2	0 - 21 % vol.	± 0,2% vol.	0,1% vol.
CO_2 (calculated from O_2 level)	0 % vol. up to $(CO_2)_N$ which depends on fuel type, see Equation (1)	± 0,2% vol.	0,1% vol.
Gas temperature	0 - 1150 °C	± 1 °C (0 - 300°C) ± 1% reading (> 300°C)	0,1 °C

2.3 Conversion of ppm to mg/kWh

Literature on space heating appliances pollution levels is quite rare and pollutant emissions are regularly reported in terms of concentration (in ppm [27]) or in terms of intensity (in mg/kWh [28]). However, it is quite rare for both pieces of information to be provided. In this case, the pollutant emissions measurements are provided by the metering device in ppm (see Table 3) whereas, for comparison purposes, it would be more meaningful to express them in terms of mg/kWh. Indeed, Table 4 for example reports from literature the NOx emission levels of several space heating appliances in mg/kWh. In addition, as it has been seen in *Section 2.1 - Tested systems*, the datasheets of the tested space heating appliances only express the emissions in terms of mg/kWh. Therefore, to use those figures as references for this study, the emission measures performed in this work must be converted from ppm to mg/kWh.

For natural gas appliances, this can be performed for carbon monoxide emissions thanks to Equation (1) [14]:

$$CO_{(mg/kWh)} = 1.074 \times CO_{(ppm)} \times \frac{(CO_2)_N}{(CO_2)_M} \quad (1)$$

Where $CO_{(mg/kWh)}$ is the carbon monoxide emissions level per unit of energy (kWh) that must be established for the studied combustion test; $CO_{(ppm)}$ is the measured carbon monoxide concentration at the exhaust of the system during the combustion test (in ppm); $(CO_2)_M$ is the measured carbon dioxide concentration at the exhaust of the system during the combustion test (in %) and $(CO_2)_N$ is the maximum carbon dioxide concentration of the dry, air-free, combustion products (in %), which depends only on the natural gas type that is fed to the studied system during the combustion. $(CO_2)_N$ is equal to 11.7% for G20 natural gas and 11.5% for G25 natural gas [14].

Indeed, in Belgium [29] (as in France or Germany [30]), natural gas comes from different sources, which implies different gas compositions and different HHV and leads to the appellations ‘lean’ and ‘rich’ gas, respectively for the natural gas source providing the lower and the higher HHV [31]. Lean gas is also called ‘L-gas’ [32], ‘type L’ gas [29] or G25 [30] whereas rich gas is also called ‘H-gas’ [32], ‘type H’ gas [29] or G20 [30]. The type of gas provided on the grid only depends on the localization of the delivery point. All lean gas deliveries are supposed to be progressively replaced (in Belgium) by 2030 by rich gas deliveries [32].

As reported in the previous section, $(CO_2)_M$ and $CO_{(ppm)}$ are provided by the meter used in this work. Also, in Equation (1), the 1.074 constant is the unit conversion coefficient related to CO emissions from natural gas appliances [33].

Table 4. Combustion only and Life Cycle Assessment (LCA) NOx emission level reported from Energie+ [28] (website developed by the University of Louvain-la-Neuve and the Energy department of the Walloon Region, in Belgium).

Space-heating appliance	NOx range (source from 1998 : Electrabel-SPE – combustion only) mg/kWh$_{LHV}$	NOx (source from 2007 : Fondation Rurale de Wallonie - combustion only) mg/kWh$_{th}$	NOx (source accessed in 2007: Gemis 4.5 - complete LCA cycle) mg/kWh$_{th}$
Old oil-fired boiler	up to 200	Unavailable	Unavailable
Non-Low NOx oil-fired boiler	150 – 180	144	244
Low NOx oil-fired boiler	90 – 120	Unavailable	Unavailable
Old gas boiler	150 – 200	Unavailable	Unavailable
Atmospheric gas boiler	100 – 180	Unavailable	Unavailable
Modulating gas condensing boiler	20 – 90	144	140
Old log wood boiler	Unavailable	180	Unavailable
Modern log wood boiler	Unavailable	151	235
Wood chip boiler (wood chips)	Unavailable	162	Unavailable
Condensing wood boiler (pellets)	Unavailable	Unavailable	344

Similarly, ppm to mg/kWh conversion for NOx emissions of natural gas appliances is obtained thanks to Equation (2) :

$$NOx_{(mg/kWh)} = \frac{\left(C_g \times NOx_{(ppm)} \times \frac{(CO_2)_N}{(CO_2)_M}\right) - 0.85(20 - T_m) + \frac{0.34(h_{m-10})}{1-0.02(h_{m-10})}}{\left(1 + \frac{0.02(h_{m-10})}{1-0.02(h_{m-10})}\right)} \quad (2)$$

Where $NOx_{(mg/kWh)}$ is the nitrogen oxide emissions level per unit of energy (kWh) that must be established for the studied combustion test; C_g is the unit conversion coefficient related to NOx emissions from natural gas appliances [34] and is equal to 1.764 for G20 (rich gas) or 1.767 for G25 (lean gas) [14]; $NOx_{(ppm)}$ is the sum of the measured nitrogen dioxide and nitric oxide concentrations at the exhaust of the system during the combustion test (in ppm); $(CO_2)_N$ and $(CO_2)_M$ have already been described for Equation (1); T_m is the temperature of the outdoor air used for the combustion (in °C) and h_m is the absolute humidity of the outdoor air used for the combustion (in g of water per kg of dry air). h_m is the only variable of Equation (2) that is not provided by the combustion analyser meter (see Table 3). By assimilating inlet air to humid air of relative humidity between 40 and 80%, at atmospheric pressure and at the T_m temperature, h_m can be approximated with the Engineering Equation Solver (EES) software. It is worth mentioning for Equation (2) that the allowable ranges for T_m, h_m $NOx_{(mg/kWh)}$ and are respectively 15 - 25 °C, 5 - 15 g of water per kg of dry air, and 50-300 mg/kWh. However, industrial partners in this work advise to use Equation (2) anyway even if some parameters are out of those ranges.

 https://doi.org/10.52202/069564-0104

The European standard from which Equation (1) and Equation (2) are deduced [14] unfortunately does not provide any information about SO_2 emissions conversion. Fortunately, another reference [35] provided Equation (3), which has been reported to be relevant not only for SO_2 but also for CO and NOx emissions, giving similar conversion results respectively to Equation (1) and Equation (2) (in its allowable range).

$$PEI_{(mg/kWh)} = F \times PEC_{(ppm)} \times \frac{20.9}{20.9-(O_2)_M} \quad (3)$$

Where $PEI_{(mg/kWh)}$ is the pollutant emissions intensity, i.e. the emission level per unit of energy (kWh) that must be established for the studied combustion test; F is an emission rate conversion factor that depends on the pollutant (and the type of fuel) and that is given in Table 5, $PEC_{(ppm)}$ is the measured pollutant emissions concentration at the exhaust of the system during the combustion test (in ppm) and $(O_2)_M$ is the measured oxygen concentration at the exhaust of the system during the combustion test (in %). Equation (3) has the particularity to consider O_2 concentration (in %) in the exhaust whereas Equation (1) and Equation (2) rely on CO_2 concentration (in %).

Similar conversion equations for diesel engine have not been reported in this paper but can also be found in literature [36].

Table 5. Natural gas F coefficients for Equation (3) depending on the pollutant type [35].

Pollutant	F mg/(kWh-ppm)
CO	0.974313
NOx	1.608389
SO_2	2.242466

3. Testing procedure and results

The end of the probe of the ‘Multilyzer STx’ must be placed at the centre of the exhaust gas chimney (or tailpipe) and the probe axis can either be oriented in the perpendicular plane of this chimney (or tailpipe) or parallel to it (if the measurements are conducted at the exit of the chimney/tailpipe). The probe disposes of a conical adjustable mechanical stop to ensure the correct probe depth to the centre of the chimney (see Figure 3).

The studied PEMFC system, which is composed of a PEMFC stack hybridized to a gas condensing boiler (see *Section 2.1 - Tested systems*), has the advantage of being equipped by design with a small, sealable access hole, fitted with a cap, directly at the exhaust of the system (in the first 5 cm of the chimney). There is thus no need with the PEMFC system to place the combustion analyser meter at the exit of the chimney, which access is very often difficult and potentially risky if it figures on the roof of the building. However, some measurements have still been taken at the exit of the chimney for comparison purposes (with the probe fully inserted in the chimney). Indeed, temperature (which varies all along the double walled chimney that cools down the flue gases and heats up the inlet air from outdoors) is not only known to influence the NO_x formation but also the NO-NO_2 equilibrium. This is especially the case in the near-post-flame zone [37] (close to the outlet of the system), but also in the atmosphere in the presence of Volatile Organic Compounds (close to the exit of the chimney) [38], which can be co-emitted in hydrocarbons combustion [37]. The PEMFC hybrid system was tested in two separate modes : with only the PEMFC turned on and with only the gas condensing boiler turned on. This system, installed in 2019, was tested in a field-test application (in a real house) in Huy (in Belgium). At the moment of the tests, the whole machine has been functioning for about 15000 hours but its integrated fuel cell has only been producing electricity for about 5500 hours. It is worth mentioning that another machine of this system, which was perfectly new, was tested in a laboratory environment (see Figure 4).

The studied mCHP SOFC system does not involve any hole in its chimney by design. However, since one machine of this system was tested in laboratory facilities, a hole was manufactured at a chimney height of 50 cm (above the system flue gases outlet). This particular machine was used for two pollutant test campaigns (conducted at minimum and intermediate electrical power output, i.e. 500 W_{el} and 1000 W_{el}). This machine, installed in 2021, had already been functioning for about 6000 hours before being tested. In the laboratory facilities, the return temperature of the heat recovery circuit could be controlled [19] (which affects the exhaust gas temperature). For the other pollutant test campaign (at full rated electrical power output, i.e. 1500 W_{el}), the combustion analyser meter was placed in another configuration. It was indeed positioned at the exit of the chimney (and fully inserted in it) since this campaign was performed on another SOFC machine (with the same reference) in a field-test application in Riemst (Belgium). At the moment of the pollutant measurements, this second machine, installed in 2017, has already been functioning for about 45000 hours.

As mentioned in *Section 2.1 - Tested systems*, another classical gas condensing boiler has been tested (only at the exit of its chimney, with the probe fully inserted in it). This system was tested in a field-test application in Riemst (Belgium).

At last, the Euro 6 diesel vehicle was tested at the exit of both of its tailpipes. The probe of the sensor could be oriented parallel to the tailpipe so it has either been fully inserted in the tailpipe (about 35 cm before its exit) or only inserted over about 15 cm. The purpose was to see the changes in the exhaust gas temperature and their impact on the pollutant measurements. It is worth mentioning that the car engine was tested at idle (±850 rpm) and at 1500 rpm but the clutch was always disengaged.

All the tests include a purge with clean air before starting the measurements. It is indeed a mandatory step requested by the 'Multilyzer STx' combustion analyser meter. At last, the sample time was always of one second.

All the tests have other specificities in the way they have been conducted and those are reported accordingly in Table 6 along with the pollutant emissions results.

In addition, for information, a graphical example of such similar pollutant tests (performed with the same sensor) is given in Figure 4 for the studied PEMFC system in its startup phase (with the boiler turned off). In that test, no NOx nor SO_2 could be measured. Startup phase (duration between the machine's startup initiated thanks to a thermal demand and the moment when the fuel cell starts producing electricity) takes about 7 min whereas the total duration to reach steady-state is about 15-20 min (gradually from 0 W_{el} to its nominal output power of 750 W_{el}). A CO peak of about 2 minutes, with a maximum at 55 ppm, can be noticed at the beginning of the power and heat generation phase, probably due to transient behaviours of the internal reformer required for this PEMFC fed by natural gas [11]. The stepped behaviour of the CO_2 percentage measurement is explained by the resolution of the sensor and the fact that it is not directly measured but established by the combustion analyser from O_2 measurements (Table 3). However, the CO_2 sudden peak is probably an outlier as it could not be explained.

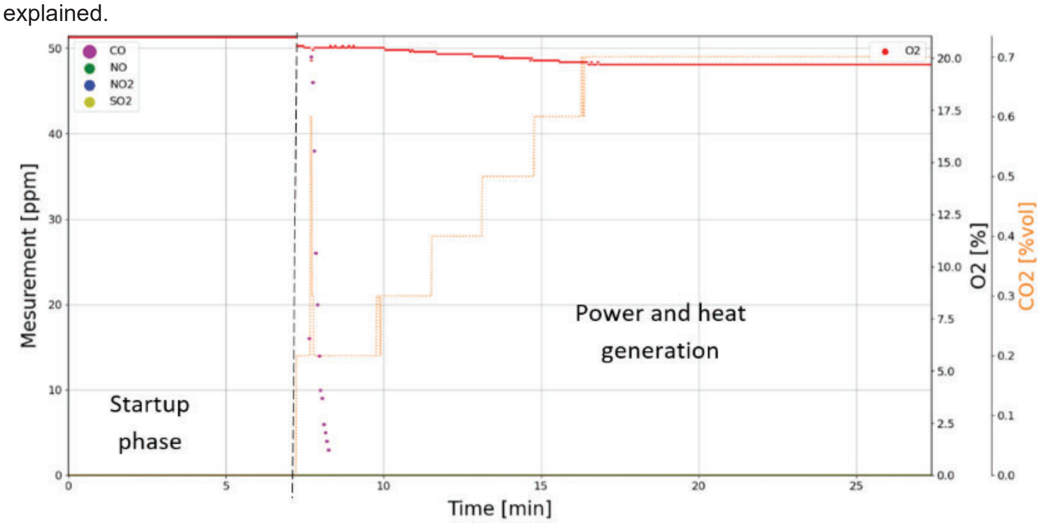

Figure 4. Pollutant measurements of the fuel cell (only) startup phase of the PEMFC-gas condensing boiler hybrid system (performed in a laboratory environment).

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Table 6. Pollutant emissions measurements results (in all tests, the sensor indicated 0 ppm of SO_2 emissions).

Test and conditions	NO [a]	NO_2 [a]	CO [a]	Remarks
PEMFC hybrid system (**PEMFC only mode**) Measured on the field-test site in Huy without control on the return temperature (or on the exhaust gas temperature)	0	0	- Startup : short peak up to 55 ppm for 2 min (in total). Also measured in the laboratory (Figure 4). - Steady state : 0 but an unexplainable short peak similar to FC startup has been measured while the PEMFC was running	- Boiler turned down by closing the radiator valves in the house - No difference in the pollutant measurement between the exit of the chimney (on the roof) and the exit of the system
PEMFC hybrid system (**condensing gas boiler only mode**) Measured on the field-test site in Huy without control on the return temperature (or on the exhaust gas temperature)	- Startup : peak up to 7 ppm for 5 min (in total) - Steady state : 0	- Startup : 3 ppm - Steady state : 3 ppm, i.e. 6.7 mg/kWh	- Startup : short peak up to 80 ppm for 30 sec (in total) - Steady state : 30 ppm, i.e. 40.7 mg/kWh	- Boiler turned on by opening the radiator valves in the house and setting a high temperature setpoint on the thermostat (the PEMFC happened to be turned off, probably conducting a regeneration procedure [11])
SOFC – 500 and 1000 W_{el} output Tested in laboratory with different heat recovery temperatures, i.e. different exhaust gases temperature (from 45°C to 25°C)	0	0	5 ppm (at 500 W_{el}), i.e. 28.3 mg/kWh 11 ppm (at 1000 W_{el}), i.e. 41.5 mg/kWh	- Return temperature of the heat recovery circuit has no influence on the pollutant measurements - Only steady state data (the system in supposed to be turned on continuously and the startup test was not conducted)
SOFC - 1500 W_{el} output Measured on the field-test site in Riemst with only one heat recovery temperature corresponding to 60°C of exhaust gases temperature	0	0	8 ppm, i.e. 17.0 mg/kWh	- Same reference but a different system as the previous row) - Only steady state data (the system in supposed to be turned on continuously and the startup test was not conducted)
Classical gas condensing boiler - high DHW load (exhaust gases temperature of about 65°C at the exit of the chimney) Measured on the field-test site in Riemst	- Startup : peak up to 8 ppm for 2 min (in total) - Steady state : 5 ppm, i.e. 10.1 mg/kWh	- Startup : peak up to 4 ppm for 2,5 min (in total) - Steady state : 2 ppm, i.e. 4.1 mg/kWh	- Startup : peak up to 50 ppm for 2 min (in total) - Steady state : 10 ppm, i.e. 12.3 mg/kWh	- No remark
Classical gas condensing boiler - low temperature space heating load (exhaust gases temperature of about 30°C at the exit of the chimney) Measured on the field-test site in Riemst	- Startup : Untested - Steady state : 0 ppm	- Startup : Untested - Steady state : 0 ppm	- Startup : Untested - Steady state : 8 ppm, i.e. 10.7 mg/kWh	- No remark
Euro 6 Diesel Engine at idle, i.e. ±850 rpm (car in neutral)	- Startup : continuous increase for about 20 min up to 60 ppm - Steady state : 55 ppm, i.e. 238 mg/kWh [36]	0	- Startup : rapid increase for about 3 min to the 200-300 ppm range - Steady state : 200-300 ppm, i.e. 800-1200 mg/kWh [36]	- The probe must be fully inserted in the tailpipe to record pollutant emissions - There is no difference between the left and right tailpipes
Euro 6 Diesel Engine at 1500 rpm	- Startup : unavailable (engine already warmed up) Steady state : 40 ppm, i.e. 173 mg/kWh [36]	0	- Startup : unavailable (engine already warmed up) Steady state : 850 ppm, i.e. 3430 mg/kWh [36]	- The probe must be fully inserted in the tailpipe to record pollutant emissions - There is no difference between the left and right tailpipes

[a] Equation (3) has been used to convert ppm measurement into mg/kWh for steady-state measurements only (of natural gas appliances). The similar conversion law for diesel engines comes from literature [36]. Peaks and startups have highly transient dynamic behaviours both on the pollutant concentration and the O_2 percentage signal, making the ppm to mg/kWh conversion hazardous.

https://doi.org/10.52202/069564-0104

4. Discussion and conclusion

None of the tested systems (PEMFC, SOFC, gas condensing boilers and Euro 6 diesel engine) showed any SO_2 emissions. This is either an indication of an issue with the SO_2 sensor or it proves the efficiency of the desulphurization treatment implemented in the natural gas process before it enters the grid [11]. In addition, both fuel cell systems include desulfurisers in their respective fuel processors according to the consulted manufacturer's documentation. Regarding the diesel vehicle, the lack of SO_2 emissions could be explained by low sulphur content of diesel in EU, limited to 10 ppm according to the EN 590:2009 regulation [39]. It could also be explained by the oxidation of SO_2 into SO_3 (not measured by the sensor) in the selective catalytic converter used in the exhaust of the engine to reduce NOx emissions [40].

Both fuel cell systems (PEMFC and SOFC) do not show any NOx emissions even if they involve high temperature reforming processes [3, 11]. Oppositely NOx emissions of gas boilers (in steady state) were measured between 3 and 7 ppm, which is rather low. Using Equation (3) and thus considering the O_2 percentage measurement (not shown in Table 6), those figures can be converted in the 6.7-14.2 mg/kWh range, which is slightly better than literature provided (see Table 4). The lower part of that range, i.e. 6.7 mg/kWh, corresponds to the gas boiler of the PEMFC hybrid system, and it is indeed under the 7.2 mg/kWh figure announced by the manufacturer. For the other classical gas condensing boiler, it is also under the announced value of 20 mg/kWh (see *Section 2.1 - Tested systems*). In comparison, the diesel Euro 6 engine showed NOx concentration of 55 ppm in neutral and 40 ppm at 1500 rpm (without any load since the clutch was not engaged). Considering another conversion equation from ppm to mg/kWh provided by literature for diesel engines [36] (Equation (3) and the coefficients of Table 5 being only relevant for natural gas appliances) and a molar mass of NO of 30, these NOx emission concentrations corresponds to the 173-238 mg/kWh range, i.e. under but close to the maximum NOx Real Driving Emissions announced at about 280 mg/kWh, assuming an average consumption of 6L per 100 km (see *Section 2.1 - Tested systems*). It also approximately corresponds to the emissions of an old oil-fired boiler (Table 4).

For all tested systems, the NO_2 emissions are either nil or quite low compared to NO emissions, which was expected as NO has been reported to be the predominant nitrogen oxide emitted by combustion devices [37].

There were no CO emissions regarding the steady state operating conditions of the PEMFC system (other than an explicable peak that is similar to the transient CO peak that occurs at the PEMFC startup, as seen in Figure 4). This was expected since CO is a major pollutant of PEMFC stacks and since it has been reported that the system is equipped with a CO removing apparatus in the fuel (natural gas) processing system (prior to the stack) [11]. Transient CO peaks are surely not caused by the fuel cell stack but by the fuel processor of the PEMFC system. For example, it could happen when the reforming processes start and is not yet at its steady state temperature levels, impeding the CO remover to operate efficiently. During these transients for which CO can occur, the PEMFC stack must indeed surely be bypassed [11]. Also, it has been reported that the PEMFC system involves an afterburner for reforming purposes (because methane reforming requires temperatures much higher than the one occurring in the PEMFC stack) [11]. In addition to burning the stack exhaust gases when the PEMFC is running (the anode exhaust still contains unused hydrogen and the cathode contains an excess of air, which is at a higher temperature that the ambient air), this afterburner also requires a direct feed from the natural gas supply to ensure enough heat for the reforming processes [11]. The inexplicable CO peak while the PEMFC was running is likely to be related to this afterburner (after the stack) and it can once again be assumed that no CO has gone through the PEMFC stack.

Oppositely, the SOFC system (two different machines of the same reference tested) showed slight CO emissions (5 ppm, 11 ppm and 8 ppm respectively at 500 W_{el}, 1000 W_{el} and 1500 W_{el} of power output) with no dependence on the thermal output or on the exhaust gases temperature (driven by the return temperature of the heat recovery system). Through Equation (3), these CO concentrations respectively correspond to 28.3 mg/kWh, 41.5 mg/kWh and 17.0 mg/kWh. It is worth mentioning that the PEMFC system was mainly tested in field-test real applications so the return temperature (and the exhaust gas temperature) could not be controlled, although it is not believed to affect the pollutant emissions in steady state (which were nil).

CO emissions peak (between 50 and 60 ppm) at gas condensing boilers startup is probably due to the momentary incomplete combustion in this highly transient starting process. In steady-state, the tested machines showed 8 to 30 ppm of CO emissions, corresponding to 10.7 mg/kWh to 40.7 mg/kWh using Equation (3) (very similar to CO emissions range of the SOFC). The gas condensing boilers were tested

 https://doi.org/10.52202/069564-0104

in field-test applications so the return temperature (and therefore the exhaust gases temperature) could not be controlled. Regarding the diesel engine, the steady state CO emissions were much higher, between 200 and 300 ppm at idle and up to 850 ppm at 1500 rpm. Equation (3) and the coefficients of Table 5 can only be used with natural gas. Therefore, another conversion law has been found in literature [36], which leads to the 800-1200 mg/kWh range at idle and to about 3430 mg/kWh for the 1500 rpm test. Those levels of CO emissions are far greater than the one announced on the certificate of conformity for the average NEDC (calculated in this work to about 145 mg/kWh, as seen in *Section 2.1 - Tested systems*). This is another proof of the inadequacy of the NEDC to account for pollutant emissions [41] but it also should be reminded that maintaining the engine at 1500 rpm while keeping the vehicle stationary is also not exactly representative of real driving conditions (although it provides interesting results for comparisons).

As a final conclusion, both tested residential fuel cell technologies fed by natural gas can be considered clean in terms of SO_2 and NOx emissions. In addition, the CO emissions can be considered quite low for the tested SOFC and even nil for the tested PEMFC. Those statements apply even with machines that have already been running for up to 45000 hours. Therefore, the biggest issue of natural gas fuel cell technologies still lies in the CO_2 emissions associated with the fossil fuel they consume.

Nomenclature

(m)CHP (Micro-)Combined Heat and Power

DHW Domestic Hot Water

GHG GreenHouse Gases

HHV (LHV) High (Low) Heating Value

LCA Life Cycle Assessment

NEDC New European Driving Cycle

PEMFC Proton Exchange Membrane Fuel Cell

SOFC Solid Oxide Fuel Cell

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