DEMOSOFC

Project n° 671470

"DEMOnstration of large SOFC system fed with biogas from WWTP"

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Analysis of the emissions from the DEMO 2nd part

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Abstract:

Emissions from two SOFC systems manufactured by Convion were measured. The measurements were carried out by VTT Technical Research Centre of Finland on 12/2017 and Eurolab, Turin on 10/2020. The main results are that no NOx and SOx was detected, particulate emissions were 0.01 mg/m^3 and CO-emissions were 7…9 mg/m^3. Therefore it can be concluded that the SOFC units operating with waste water treatment gas had very low emissions. The work on emission measurements of SOFC systems will continue in FCH JU funded project Comsos (https://www.comsos.eu/).

Keyword list:

SOFC, biogas, demonstration, efficiency, emissions, SOx, NOx, CO, particulate

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1 Methods

1.1 On-site emission measurements on 12/2017 (SOFC unit #1)

1.1.1 Overview

On-site emission measurements from the first installed C50 unit were measured using a laboratory-in-a-van approach. All the measurement equipment, computers, calibration gases, etc. were installed into a van and the van was driven to the Società Metropolitana Acque Torino S.p.A. (SMAT) Collegno site in Turin, Italy. This is a standard approach at VTT when measuring emissions from different power-production plants and it allows for dedicated and custom-made setups to be used on-site with relative ease. Figure 2 shows the site with Convion C50 unit #1 at the front and VTT's van with all the measurement equipment behind it.

Figure 1 shows the simplified measurement setup. A heated sampling line was placed inside the C50 units exhaust chimney. The extracted gas was then fed through separate sampling line to Fourier Transform InfraRed (FTIR) analyzer for measuring gaseous species and to Electronic Low-Pressure Impactor (ELPI) for particulate measurement. The sample flow to ELPI was diluted with bottled air using ratio of 1:7.

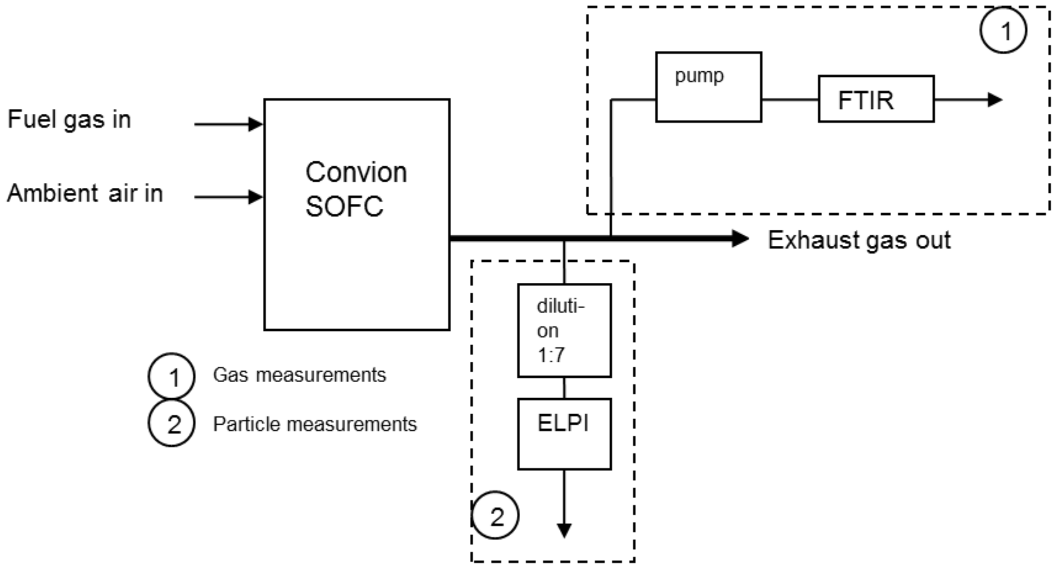

Figure 1. Process diagram of the emission measurement setup.

Figure 2. Setting up emission measurements. Convion C50 system in the front with VTT van with all the emission measurement equipment behind it.

1.1.2 Particulate measurement

Particle number size distributions were measured with the ELPI instrument, manufactured by Dekati Ltd. The main parts of the ELPI are charger and low pressure impactor. Inside the charger the particles are charged and the aerodynamic size classification is done inside the impactor. The current values are measured from each stage of the impactor and transformed to number of particles using calculations. ELPI measures particle size distribution and concentration in real-time of particle size range from 8 nm to 10 µm. Particle mass concentration was calculated using particle density of 1 kg/dm^3. Sampling flow from exhaust pipe was diluted to 1:7 with purified compressed air before ELPI. Background (zero) was measured at least twice a day using, HEPA-filtered air.

According to standard CEI/IEC 62282-3-200[1] the particulate concentration measurements should be performed using gravimetric method based on standard ISO 9096:2003[2]. Typical limit of quantification for this gravimetric method is 2 mg/m^3 dry gas, at Normal Temperature and pressure (NTP, 273.15 K, 1013.25 mbar). Particle concentrations in the fuel cell were expected to be significantly below this limit and therefore, particulate concentration measurements were performed using ELPI so that relevant data could be obtained.

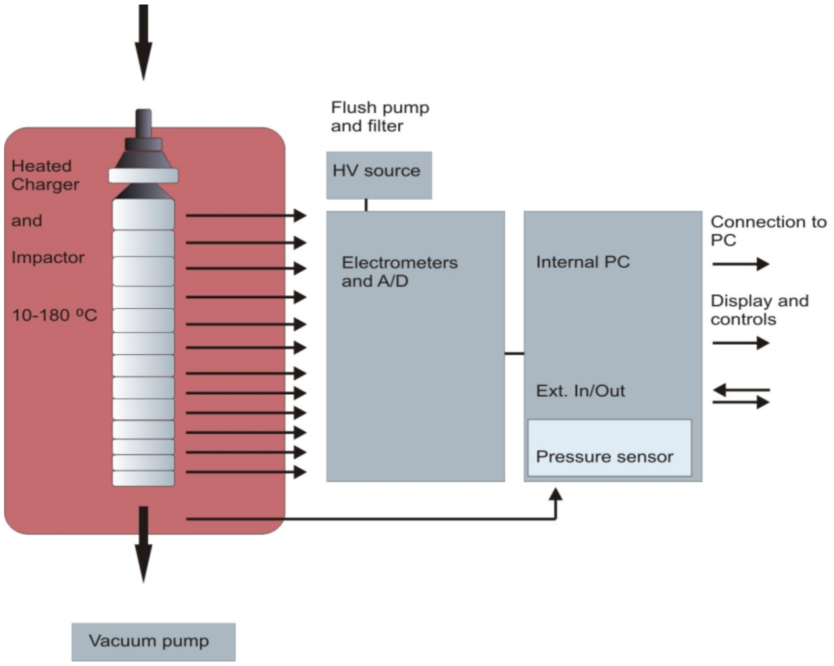

Figure 3. Measurement principle of the electronic low-pressure impactor (ELPI).

1.1.3 Gas emissions

Measured gas components were,H_2O CO_2, CO, CH_4, N_2O, NO, NO_x (as NO_2), SO_2, C_2H_6, HCHO, HF, HCl and O_2. Sampling flow through gas analysing system was three litres per minute with measuring average time of two minutes. Oxygen analysis was performed with zirconium oxide cell built-in to Gasmet Portable Sampling System. The detection limit for O_2 is 0.1 vol-%. Other gas concentrations were analysed using Gasmet Dx4000N which is based on Fourier Transform Infra Red (FTIR) –technique. Analyser's sample cell absorption length was 5 meters and temperature of the cuvette was 180 °C.

[1] IEC 62282-3-200 Fuel cell technologies –Stationary fuel cell power systems – Performance test methods.

[2] ISO 9096:2003. Stationary source emissions – Manual determination of mass concentration of particulate matter.

1.2 On-site emission measurements on 10/2020 (SOFC unit #2)

Due to the covid-19 related travel restrictions, VTT had to outsource this emission measurement campaign to company Eurolab in Turin. Eurolab carried out the measurements on 14th of October, 2020. The emission measurement campaign included measurement of gaseous species via continuous online-analysis as well as with collection to sorbents and measurement later using gas chromatography. Particle concentration was also measured with gravimetric method according to EN 13284-1:2017. Table 1 contains further details on the measurement methods. Figure 4 shows emission measurements carried out to Convion SOFC unit #2.

Figure 4. Emission measurements being carried out on 14th of October 2020.

Table 1. Analytical methods used by Eurolab to determine exhaust emissions.

Method	Description
UNICHIM 158:1988	Strategia di campionamento e criteri di valutazione
UNI EN 15259:2008	Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report
UNI EN ISO 16911-1:2013	Stationary source emissions - Manual and automatic determination of velocity and volume flow rate in ducts - Part 1: Manual reference method
UNI EN 14789:2017	Stationary source emissions - Determination of volume concentration of oxygen - Standard reference method: Paramagnetism
UNI EN 14790:2017	Stationary source emissions - Determination of the water vapour in ducts - Standard reference method
UNI EN 14791:2017	Stationary source emissions - Determination of mass concentration of sulphur oxides - Standard reference method
UNI EN 14792:2017	Stationary source emissions - Determination of mass concentration of nitrogen oxides - Standard reference method: chemiluminescence
UNI EN 15058:2017	Stationary source emissions - Determination of the mass concentration of carbon monoxide - Standard reference method: non-dispersive infrared spectrometry
UNI EN 12619:2013	Stationary source emissions - Determination of the mass concentration of total gaseous organic carbon - Continuous flame ionisation detector method
UNI EN 13649:2015	Stationary source emissions - Determination of the mass concentration of individual gaseous organic compounds - Sorptive sampling method followed by solvent extraction or thermal desorption
UNI EN 13284-1:2017	Stationary source emissions - Determination of low range mass concentration of dust - Part 1: Manual gravimetric method

2 Results and discussion

2.1 On-site emission measurements on 12/2017 (SOFC unit #1)

2.1.1 Particulate emissions

Figure 5 5 and 6 present measured particle concentration as a function of particle size. Ambient air concentrations are shown with black bars and concentrations measured from C50 system exhaust are shown with grey bars. It can be noticed that the concentrations measured from the fuel cell system exhaust are several orders of magnitude lower than the ambient particle concentration. This is caused by the very effective filtering of incoming air inside the system as well as the fact that in this aspect fuel cells as electrochemical conversion devices differ very significantly from e.g. internal combustion engines.

7 contains average ambient particulate concentrations measured on-site on 12-13th of December 2017. The ambient particulate concentrations can be considered fairly high, but it should be noted that during the time of measurement, weather was unusually cold with night-time temperatures below zero centigrade and no rainfall. These conditions in urban environment usually result in higher particulate concentrations in air. For comparison, Lonati et al. measured average particulate concentration of 25 000 1/cm^3 in Milan during winter 2003-2004[3].

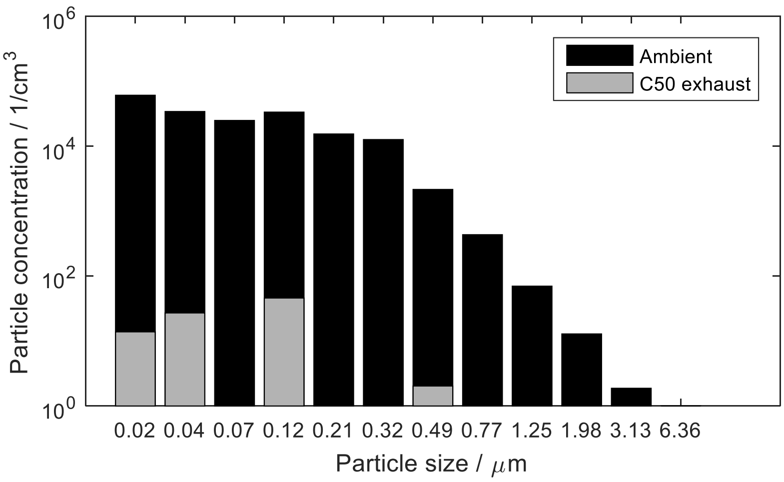

Figure 5. Particle size distribution measured from ambient air and Convion C50 exhaust.

[3] Milan, Italy 2003-2004: cold season average 25000 1/cm3, warm season average 13000 1/cm3

G. Lonati, M. Crippa, V. Gianelle, and R. van Dingenen, “Daily patterns of the multi-modal structure of the particle number size distribution inMilan, Italy,” Atmospheric Environment, vol. 45, no. 14, pp. 2434–2442, 2011.

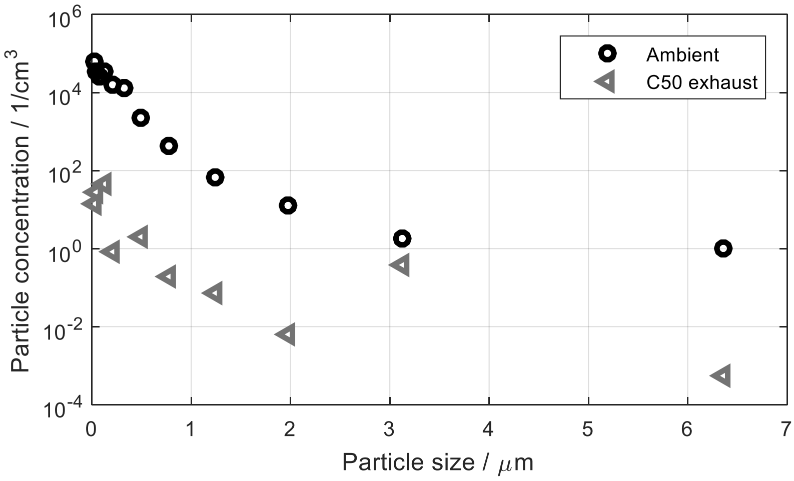

Figure 6. Particle concentration measured from ambient air and from Convion C50 exhaust.

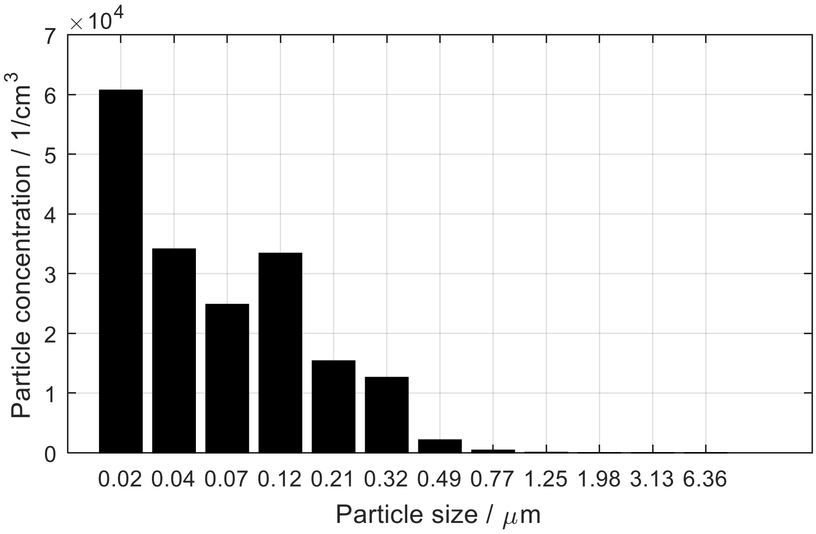

Figure 7. Measured particulate concentration in ambient air at SMAT Collegno 12-13th of December 2017.

2.1.2 Gas emissions

At nominal operating conditions, no other gaseous emissions were measured except water vapour (4.7±0.4%), CO_2 (3.4±0.2%), CO (7±2 ppm) and O_2 (18.3±1.0%). All of the other measured components were below limits of quantification (Table 2). The measurement uncertainties quoted here are based on previous uncertainty analysis carried out at VTT for similar gas matrix. In case any other emissions stated in **Errore. L 'origine riferimento non è stata trovata.** were found, a more detailed uncertainty analysis should be carried out using the procedure defined in CEN/TC 264 N 2719[4].

Figure 8 8 shows gaseous emissions during startup of the C50 fuel cell system from hot standby -state. At the start of the measurement run the system was held at hot standby-mode. Then the system was started and electrical power was ramped up. It can be noted that a peak of about five minutes in duration and maximum of 80 ppm CO is emitted. After the startup-peak, CO-level quickly drops down below quantification limit of 3 ppm.

[4] Stationary Source Emissions — Determination of mass concentration of multiple gaseous species — Fourier transform infrared spectroscopy", CEN/TC 264 N 2719 (Official CEN/TS documentation to be published during 2018).

Table 2 summarizes the measured emissions at steady-state conditions. All of the measured emissions are below quantification limits except H_2O, CO_2, CO and particles. Particle emissions are lower than the EU reference values for ambient air, so it can be concluded that SOFC technology does not increase particle pollution.

Table 2 also contains emission limits for gas engines and turbines which can be used for comparison.

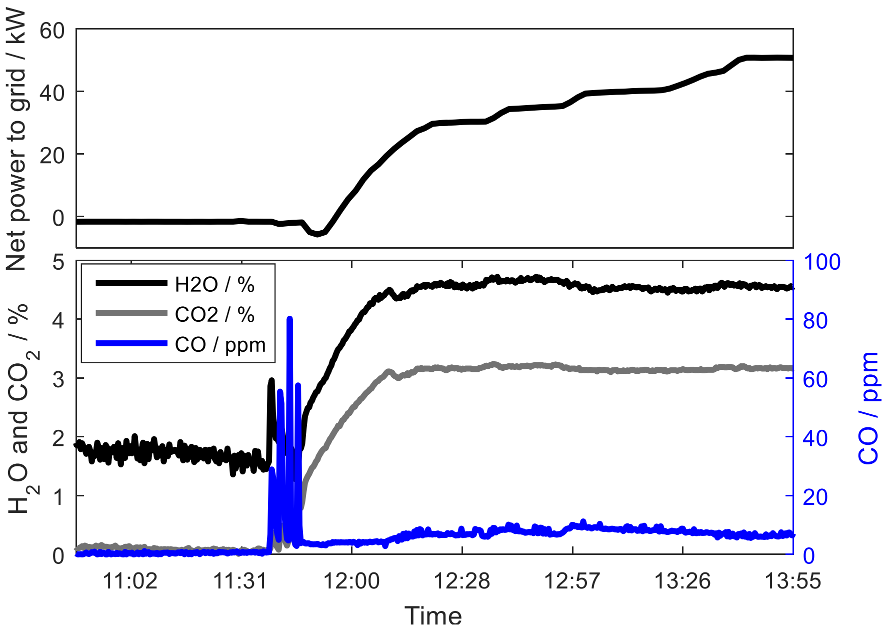

Figure 8. Gas emissions during C50 system startup.

Table 2. Summary of the measured steady-state emissions from the Convion C50 unit operated at the WWTG plant in Turin, Italy.

Species	**Unit**	**Measured value**	**Typical emission limits of gas engines and turbines**[5] [6]
H_2O	Vol-%	4.7	
CO_2	Vol-%	3.4	
CO	mg/m^3	7	100
CH_4	mg/m^3	<2	
N_2O	mg/m^3	<8	
NO	mg/m^3	<20	
NO_x (as NO_2)	mg/m^3	<20	75…200
SO_2	mg/m^3	<8	15…60
C_2H_6	mg/m^3	<14	
HCHO	mg/m^3	<7	
HF	mg/m^3	<10	
HCl	mg/m^3	<10	
O_2	Vol-%	18.3	
Particulate	mg/m3	0.01	Ambient air EU reference values[7] 0.025 (PM2.5), 0.05 (PM10)

[5] Limitation of emissions of certain pollutants into the air from medium combustion plants (MCP-directive), DIRECTIVE (EU) 2015/2193

[6] Industrial emissions (integrated pollution prevention and control) (IED-directive), DIRECTIVE 2010/75/EU

[7] Air quality in Europe — 2016 report, EEA Report No 28/2016

2.2 On-site emission measurements on 10/2020 (SOFC unit #2)

2.2.1 Results

Due to the covid-19 related travel restrictions, VTT had to outsource this emission measurement campaign to company Eurolab in Torino. Eurolab carried out the measurements on 14th of October, 2020. Table 3 contains the main results of the emission measurement campaign carried out by Eurolab from the second SOFC unit. Particle emissions, NOx and SOx as well as THC are below quantification limits of the instruments as expected. 8.6 mg/Nm3 of CO was detected. The results show 8.7 mg/Nm3 of total organic carbon (TOC) measured online with FID but <0.05 mg/Nm3 of total hydrocarbons (THC) measured with sorptive sampling method, which is a disagreement. Other measured compounds are below quantification limits.

Table 3. Emission measurement results carried out by Eurolab, Torino.

Species	Unit	Test 1 11:47 – 12:17	Test 2 12:17 – 12:47	Test 3 12:47 – 13:17	Average value	Standard deviation
Low range dust	mg/Nm^3	< 0.3	< 0.3	< 0.3	**< 0.3**	___
TOC	mg/Nm^3	9.7	9.0	7.3	**8.70**	1.2
THC	µg/Nm^3	< 50	< 50	< 50	**< 50**	___
O_2	Vol-%	18.7	18.7	18.7	**18.7**	___
NOx	mg/Nm^3	< 0.3	< 0.3	< 0.3	**< 0.3**	___
CO	mg/Nm^3	8.6	8.6	8.5	**8.6**	0.1
SOx	mg/Nm^3	< 0.3	< 0.3	< 0.3	**< 0.3**	___
Temperature	°C	___	___	___	**56**	___
Water vapour	Vol-%	___	___	___	**3.9**	___

3 Summary

The main findings regarding emissions from the Convion C50 SOFC units operated with biogas from waste water treatment are summarized in Table 4. Due to the covid-19 travel restrictions, an identical set of measurements could not be replicated on both units as VTT needed to outsource emission second emission measurements to Eurolab. However, the emission measurements of different SOFC units will continue in FCH JU funded project Comsos[8], thus providing further insights to emissions of SOFC units.

It can be noted that the exhaust gas is very clean and contains less particulate than typical urban ambient air and only 7…9 mg/Nm^3 of CO. No SO_2 or NO_x was detected. Therefore it can be stated that these results from the DEMOSOFC units highlight the emission reduction potential of SOFC technology compared to conventional power production methods from biogas.

Table 4. Main findings from the emission measurement campaigns carried out during DEMOSOFC project. Emissions in mg/kWh are based on estimated (not measured) exhaust flow and therefore are subject to relatively large uncertainty.

Emission	Unit	Measured value / mg/m^3	SOFC #	Power at measurement time / kWe	mg/kWh	Typical emission limits of gas engines and turbines[9][10]
CO	mg/m^3	7	1	50	60	100 mg/m^3
		9	2	32	116	
CH_4	mg/m^3	<2	1	32	-	
NO_x	mg/m^3	<20	1	50	-	75…200 mg/m^3
		<0.3	2	32	-	
SO_2	mg/m^3	<8	1	50	-	15…60 mg/m^3
		<0.3	2	32	-	
Particulate	mg/m^3	0.01	1	50	0.8	Ambient air EU reference values[11] 0.025 (PM2.5), 0.05 (PM10)
		<0.3	2	32	-	

[8] https://www.comsos.eu/

[9] Limitation of emissions of certain pollutants into the air from medium combustion plants (MCP-directive), DIRECTIVE (EU) 2015/2193

[10] Industrial emissions (integrated pollution prevention and control) (IED-directive), DIRECTIVE 2010/75/EU

[11] Air quality in Europe — 2016 report, EEA Report No 28/2016

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