

Catalytic Wall Flow Filters for the Reduction of Biomass Boilers Emissions

Giovanni Stoppiello^{*a}, Vincenzo Palma^b, Francesca Hugony^a, Eugenio Meloni^b, Maurizio Gualtieri^a

^aENEA, Unità Tecnica Tecnologie Saluggia (UTTS), Strada per Crescentino 41, 13040 Saluggia (VC), Italy

^bDip. di Ingegneria Industriale, Università degli Studi di Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy
 giovanni.stoppiello@enea.it

Biomass is worldwide available and the interest in it as energy source has been increased in the recent years, with the aim to reduce the fossil fuels dependence and to increase energy supply in developing countries. Nevertheless, biomass combustion emissions put some concerns for its environmental acceptance, particularly for carbon monoxide (CO), polycyclic aromatic hydrocarbons (PAHs), and particulate matter (PM) contents, which must be reduced to meet the current environmental limits. Among the different technologies for the abatement of these pollutants, wall flow filters may represent an efficient solution since they allow to combine physical filtration processes for particles removal and catalytic oxidative reactions for solid and gaseous pollutants treatment. In this work, two different types of wall flow filters, respectively made of silicon carbide (SiC) and alumina (Al₂O₃), have been tested directly at the exhaust of a 30 kW nominal power conventional pellet boiler. The two samples were chemically and structurally characterized before testing. From the first set of experiments, the SiC filters, specifically loaded with 15 %wt and 25 %wt copper ferrite (CuFe₂O₄) as catalyst, proved to be more suitable for the aim of this research, since they allow to simultaneously reduce CO and PM emissions of about 95 % and 92 % respectively. Different filters geometries, fitting locations inside equipment and new active species deserve further investigations.

1. Introduction

While the traditional fossil fuels reserves are slowly running out, the demand for alternative renewable energy sources like biomass, which currently contribute about 13 % of the world energy supply, is constantly growing (Khan et al., 2009). In many European Countries, the advances in technology and treatment of wood biomass have allowed this type of fuel to become an important alternative to traditional fossil fuels in CHP and small scale heating plants, in terms of ease of use, energy efficiency and reduction of CO₂ emissions (Verma et al., 2009). However, various studies have shown that the combustion of biomass, especially in small scale heating systems, is the source of both particulate matter (PM, with average size < 1 μm) (Verma et al., 2011) and gaseous pollutants, such as polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), carbon monoxide (CO) (Tissari et al., 2008), nitrogen oxides (NO_x) and sulphur oxides (SO_x) (Kubica et al., 2007). In addition, besides the health effects on population (Lighty et al., 2000) and environment (Van Loo and Koppejan, 2002), PM influences the reliability and efficiency of heating systems, because of its deposition on the internal surfaces of the plants, causing corrosion, fouling and reduction of heat exchange (Tissari et al., 2008). In this work, the performances of two different types of wall flow filters, respectively made of silicon carbide (SiC) and alumina (Al₂O₃), have been tested directly at the exhaust of a 30 kW nominal power conventional pellet boiler, with regards to PM and CO abatement. As showed in recent studies the geometry of these filters allows to high PM removal efficiencies (Palma et al., 2011) when employed in catalytic filtration systems of soot particles from diesel engines, at catalyst loads up to 15%wt (Palma et al., 2012) and 20%wt (Palma et al., 2013). Based on these premises, and minding the significant differences between the two types of gas to be treated, the SiC wall flow filters were identified as good candidates for experimentation, with the goal to develop a system able to simultaneously reduce PM and CO emissions.

2. Materials and Methods

2.1 Filter elements

Two different types of wall flow filters, respectively made of SiC and Al₂O₃, have been prepared for the present activity. Alumina filters were initially considered as ceramic materials with pores sizes of the same order of magnitude of PM from biomass combustion applications. They were prepared by extrusion of 60 % and 92 % alumina slurry phases through appropriate mold geometry, and subsequent heating at high temperature for final sintering. The catalytic SiC filters were made by using commercial Pirelli Ecotechnology SiC wall-flow monoliths with 150 cpsi, loaded with different wt-percentages of copper ferrite (CuFe₂O₄) as catalyst. The filters were suitably shaped (diameter 26 and 30 mm, length 125 mm), as showed in Figure 1, and they were wrapped in an heat expanding intumescent ceramic-mat (Interam, 3M), in order to be enclosed in the sampling line at the exhaust of the biomass boiler (Figure 2). Preliminary activity tests were carried out comparing the performances of the bare monoliths and investigating the behavior of 15 %wt and 25 %wt CuFe₂O₄ loaded SiC filters.

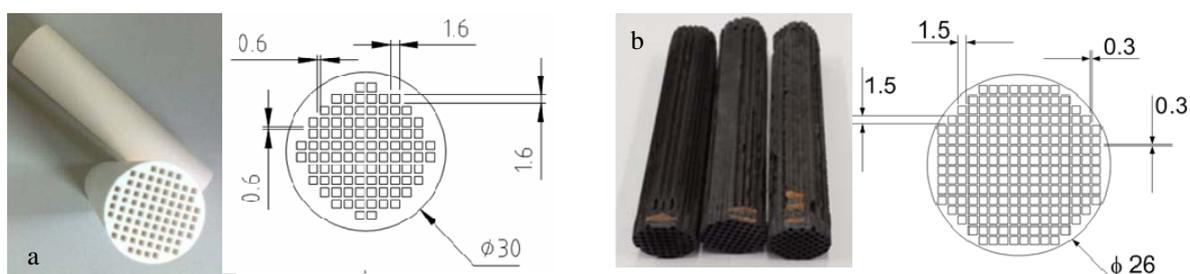


Figure 1: shape and dimensions of Al₂O₃ (a) and SiC (b) wall flow filters

2.2 Characterization of porous and catalytic materials

Both SiC and Al₂O₃ filters were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDAX), porosimetry tests, TG-DTA analysis, and Temperature Programmed Reduction (TPR) analysis. CuFe₂O₄ was prepared starting from iron nitrate (Fe(NO₃)₃·9H₂O) and copper nitrate (Cu(NO₃)₂·3H₂O), mixed in a 2:1 molar ratio in distilled water, continuously stirred at 60 °C. The catalytic filters were prepared by repeated impregnation steps of SiC wall-flow monoliths in the prepared solution for 30 minutes, drying at 60 °C for 9 hours and calcination at 1000 °C for 30 minutes after each impregnation, in order to achieve a uniform distribution of the active species (Palma et al., 2012). Filters were loaded with different amounts of catalyst: 15, 20, 25 and 30 %wt, determined by comparing the weights of the catalytic filters in respect with the bare filters one. The prepared powder of CuFe₂O₄ was characterized by X-Ray Diffraction (XRD) and TG-DTA analysis. Results of XRD analysis showed the presence of the typical peaks of CuFe₂O₄ in its tetragonal and cubic form (Palma et al., 2012).

2.3 Test facility and operating conditions

The experimental tests on ceramic wall flow filters were carried out by using a KWB Multifire USV V 30 biomass heating system, fuelled with certified (UNI EN 14961-2) wood pellet. The nominal power of this plant is 30 kW and the fuel consumption at full load is about 7 kg/h. The filters were tested in a derivation column where part of the flue gases (about 8 NI/min) was conveyed (Figure 2). The column was externally heated by a 3,0 kW tubular furnace in order to set the filters temperature at the desired values. Pressure drops through the filters were measured by a U-tube water manometer (-500/+500 mmH₂O). PM content of still hot gases (about 190 °C) was gravimetrically measured downstream the column by a PM10 DEKATI 3-stages impactor that allows to sample solid particles on plane aluminum and glass-fiber filters in the following size ranges: PM >10 μm; PM = 2.5–10 μm; PM = 1–2.5 μm; PM <1 μm. At the impactor outlet, the flue

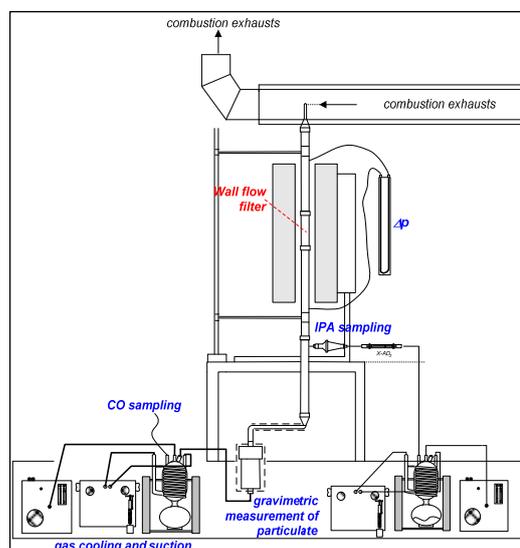


Figure 2: experimental set up

gas sampling flux was dried in an ice bath condenser and conveyed (about 2 NI/min) to the gas analyzers, which detected O₂, CO₂ and CO concentrations. O₂ concentration was measured by means of a zirconium oxides based system (0-26 %; $\pm 0,2$ %), while CO₂ and CO were detected by NDIR analyzers, whose measurements ranges were respectively 0 – 15 / 20 % ($\pm 0,3$ %) and 0 – 1000 / 10000 vppm (± 20 vppm). The experimental set up was also equipped with a polycyclic aromatic hydrocarbons (PAHs) sampling line, based on cold dry adsorption of PAHs on X-AD₂ resins. Two different types of experimental tests were carried out: filtration tests of uncatalytic wall flow filters at low temperature (T ~ 160 °C), and tests at high temperature (T >400 °C) with catalyst loaded filters (at 15 %wt and 25 %wt loads) and uncatalytic samples (0 %wt). In the first case, both Alumina filters (respectively at 60 % and 92 % Alumina content) and SiC filters were examined. In the second case, only SiC filters were investigated. For Alumina filters, surface velocity was kept in the range of 0,20 – 0,30 m/s, while for SiC filters surface velocity was 0,30 – 0,40 m/s at low temperature and 0,60 - 0,70 m/s at high temperature. The duration of each test was fixed to 120 min, unless reaching critical conditions for experimental line (too high pressure drops) or filters breakings.

3. Results and discussions

3.1 Filters porosity characteristics

The porosity and the bulk density of the filters were measured by means of ACCUPYC 1300 Micrometrics and PASCAL 440 Thermo Fisher Scientific, respectively. Al₂O₃ filters showed an average pores size much lower than the SiC ones, for which the increase of CuFe₂O₄ load also led to the reduction of their average pores diameter, from 17 μ m for uncatalytic filters to 12.3 μ m for 25 %wt CuFe₂O₄ loaded ones. The results are summarized in Table 1, in which the open porosity refers to the open space divided by the total volume of porous material.

Table 1: Porosimetric characteristics of the wall flow filters

	Al ₂ O ₃ (60%)	Al ₂ O ₃ (92%)	SiC, 0% cat.	SiC, 15% cat.	SiC, 25% cat.
He density (g/cm ³)	3.90	3.97	3.2	3.3	3.5
bulk density (g/cm ³)	2.23	2.12	1.8	1.9	2.4
av. pores size (μ m)	0.62	0.56	21.2	24.6	-
open porosity (%)	43.7	46.6	44.0	43.0	29.0

3.2 SEM-EDAX results

Both uncatalytic and catalytic SiC samples were investigated by Scanning Electron Microscopy (SEM, LEO 420 V2.04, ASSING), and Energy Dispersive X-ray Spectroscopy (EDX, INCA Energy 350, Oxford Instruments, Witney, UK). The results (Palma et al., 2012) showed very homogeneous distribution of the active species on the filter surface, and from the images below it can be noted that they cover the whole surface of SiC granules. Even by increasing their load, the inner wall pores were not occluded, but there was a uniform decrease in filters pores diameter, still allowing their use as catalytic filter. In Figure 3 is reported the elements distribution as obtained by SEM-EDX element mapping for the 15 %wt CuFe₂O₄ catalytic filter.

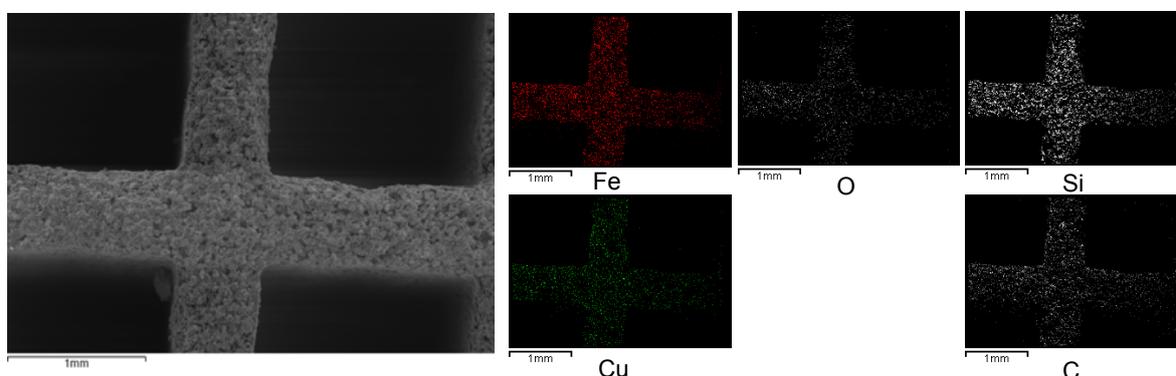


Figure 3: SEM image and distribution of elements, as obtained by EDX element mapping for the 15 %wt CuFe₂O₄ loaded filter

The elements which were evidenced by EDX are those of the structural material of the filter (C, and Si), as well as the catalyst active species (Cu and Fe). These results confirm that the procedure used for filter preparation is suitable for the homogeneous deposition of active species without any washcoats.

3.3 TG-DTA and TPR analysis

The activity of powder catalyst and catalytic filters in soot combustion reaction was evaluated by simultaneous TG-DTA analysis (SDT Q600 TA Instruments) by using soot particles as reference for the uncatalytic reaction. Samples were heated in air (flow rate = 100 Ncm³ min⁻¹) from 20 to 800 °C with an heating rate of 10 °C min⁻¹. The results for soot alone (Palma et al., 2013) show its typical combustion behavior (ignition temperature of about 550 °C and maximum reaction rate at about 620 °C), while the results for the mixture of soot and CuFe₂O₄ powder show a lower ignition temperature (380 °C), and the maximum combustion rate temperature of about 450 °C. These data confirm the high activity of the catalyst on soot oxidation. The results also show that the increase in catalyst load provides lower ignition and maximum combustion rate temperatures, and the rate of catalytic oxidation reactions increases. The H₂-TPR analysis was carried out by using a 15 %wt CuFe₂O₄ catalytic filter from room temperature to 900 °C, at an heating rate of 5 °C min⁻¹ in 5 % H₂/N₂ flow. The reaction parameters (temperature and concentrations) were monitored by an HIDEN Analytical system, coupled with a quadrupole mass spectrometer. The results (Palma et al., 2013) showed two pronounced reduction peaks at about 300 °C and 610 °C, due to the reduction of CuFe₂O₄ to Cu and Fe₃O₄, and, subsequently, the reduction of Fe₃O₄ to Fe (Kameoka et al., 2010), according to the following complete reaction:



The Cu ratio was 4.4, which is consistent with the theoretical ratio for the complete reduction of CuFe₂O₄ to Cu and Fe. This value corresponds to about 17 %wt of CuFe₂O₄, which is in a quite good agreement with the estimated 15 %wt of CuFe₂O₄ on the monolith. As shown in literature (Kameoka et al., 2005) mixture of Cu and Fe from reduction is favorable for the formation of CuFe₂O₄ at high temperature (about 800 °C in air). The TPR profile showed that the catalyst loaded monolith was able to act as a redox oxidation catalyst in the temperature range 300 – 800 °C, thanks to the presence of the homogeneous dispersion of copper ferrite.

3.4 Biomass boilers parameters and emissions

The average values of combustion exhausts properties were registered during preliminary tests (Table 2). Heating system was properly set in order to increase CO and PM concentrations in the flue gas, as to better evaluate the efficiency of pollutants abatement by the ceramic catalytic wall flow filters.

Table 2: Flue gas properties at the exit of biomass combustion plant

Temperature (°C)	O ₂ (vol %) _{dry}	Air excess - e -	PM (mg/Nm ³ 10% O ₂)	CO (mg/Nm ³ 10% O ₂)	Flow rate (Nm ³ /h)
120 - 140	~ 8	~ 0,66	90 - 110	~ 4000	75

Almost the whole content (> 95 wt%) of PM in the flue gases resulted with particle size < 1 μm (Table 3).

Table 3: Average PM contents in flue gas, by particle size distribution (gravimetric measurements)

PM < 1 (mg/Nm ³)	PM 1 – 2,5 (mg/Nm ³)	PM 2,5 - 10 (mg/Nm ³)	PM > 10 (mg/Nm ³)
93,2	3,1	1,6	-

3.5 Behavior of uncatalytic filters

The preliminary tests on wall flow filters behavior were focused on the analysis of pressure drops (ΔP) during physical filtration. For Alumina filters (pore sizes similar to PM ones), high pressure drops with unstable conditions were obtained in the case of 92 % Al₂O₃ sample (Figure 4a), while breaks of filters channels were registered during the tests of 60 % Al₂O₃ filter (Figure 4b). For SiC filters, pressure drops were regularly increased during the tests (Figure 5), in agreement with the continuous deposition of particles on the outer and inner surface of porous material. Nevertheless, by foreseeing the industrial use of catalytic wall flow filters as intermittent regenerated devices (at high temperature), pressure drops are still too high. Further investigations on ceramic materials aimed at lowering pressure drops are still carried out. The different behavior between Alumina and SiC filters is likely to be related to the different pores size of the two materials (Table 1): since particle size of emitted PM is almost totally less than 1 μm (Table 3), in the case of Alumina filters (with pores size less than 1 μm, too) only surface filtration occurs, as indicated by the excessively high pressure drops which were registered even at the beginning of the tests. On the contrary, the pores size of SiC filters is higher

than the particles one (around 20 μm against less than 1 μm), so that both surface and depth filtration processes take part during filtration. In this case, pressure drops are relatively low and the available filter surface for particle deposition is increased, allowing a more regular filtration process.

3.6 Activity of catalytic filters

Two experimental tests, respectively at 160 °C and 420 °C, were performed to check the catalytic activity of 15 %wt CuFe_2O_4 loaded SiC monoliths out, in terms of CO contents abatement from exhausts. The data of CO concentrations downstream the filters, compared with the typical CO concentrations in flue gas (tab.2) showed that at similar flue gas temperatures ($T = 160^\circ\text{C}$) copper ferrite catalyst had no activity, while at relatively high temperature ($> 400^\circ\text{C}$), it reduced CO content in flue gas more than one order magnitude, with an average abatement efficiency of about 95 % (Figure 6b). This effect can be considered constant for at least two hours. As for PM, even at temperatures lower than 550°C (typical PM oxidation temperature) the tests performed with catalyst loaded filters showed constant pressure drops during filtration (Figure 7a and 7b), and an average abatement of PM more than 92 % by gravimetric measurement. Therefore, it can be assumed that organic particles are simultaneously filtered and thermo-converted on the catalytic filter surface.

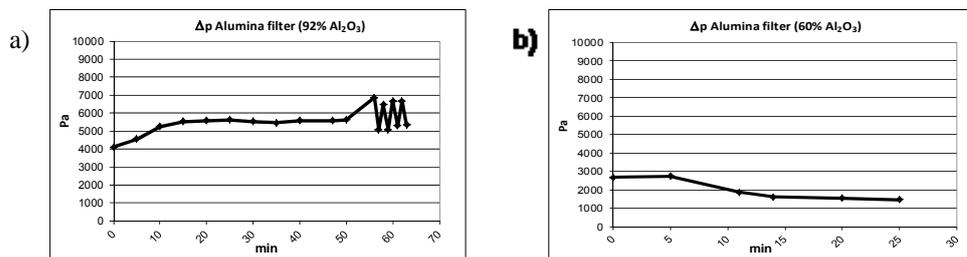


Figure 4: ΔP of Alumina filters (a: $T_f = 170^\circ\text{C}$, $v_s = 0,30\text{ m/s}$; b: $T_f = 165^\circ\text{C}$, $v_s = 0,25\text{ m/s}$)

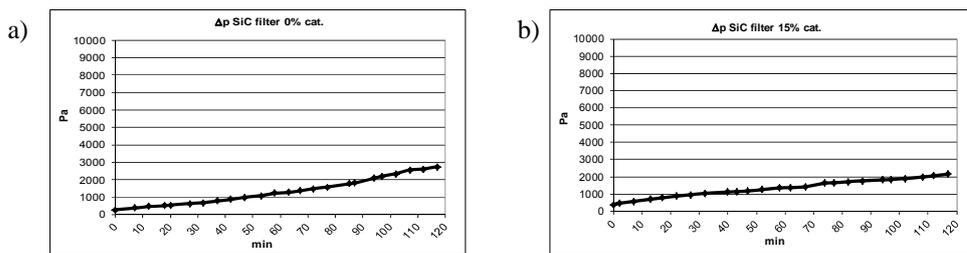


Figure 5: ΔP of SiC filters (a: 0 %cat., $T_f = 160^\circ\text{C}$, $v_s = 0,38\text{ m/s}$; b: 15 %cat., $T_f = 160^\circ\text{C}$, $v_s = 0,40\text{ m/s}$)

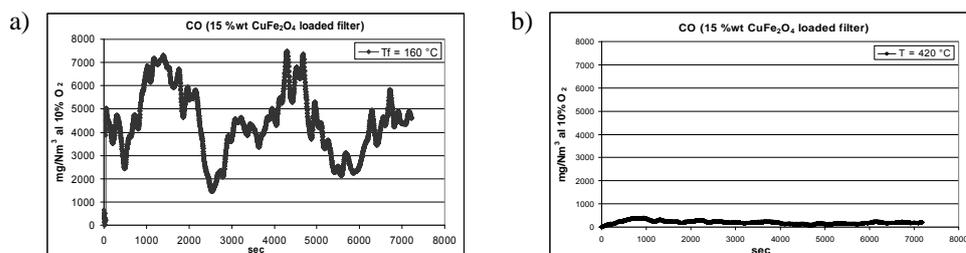


Figure 6: CO concentration (mg/Nm^3 at 10% O_2) downstream 15 %wt CuFe_2O_4 loaded filter (a: $T_f = 160^\circ\text{C}$, $v_s = 0,40\text{ m/s}$; b: $T_f = 420^\circ\text{C}$, $v_s = 0,63\text{ m/s}$)

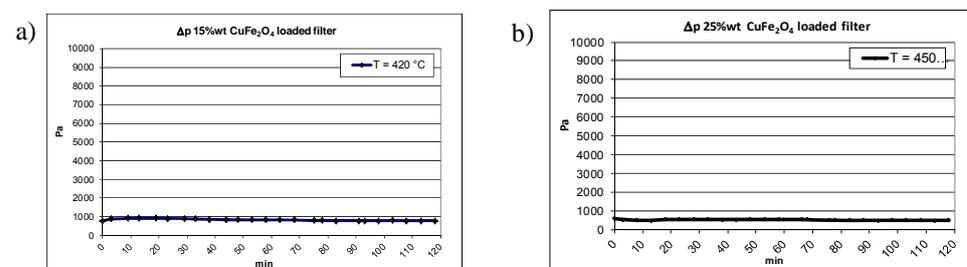


Figure 7: pressure drops for a): 15 %wt CuFe_2O_4 loaded filter ($T_f = 420^\circ\text{C}$, $v_s = 0,63\text{ m/s}$) and b): 25 %wt CuFe_2O_4 loaded filter ($T_f = 450^\circ\text{C}$, $v_s = 0,69\text{ m/s}$)

4. Conclusions

The results of the present experimental activity show that the wall flow catalytic filtration technology, previously tested in diesel engines applications, can be also successfully applied in biomass combustion systems, obtaining very high PM filtration efficiency. Since PM from biomass heating systems has particles size less than 1 micron for almost 100 %, the operation of wall flow filters is strictly dependent to their inner porosity, which must be at least one order magnitude greater than PM size. In this case, depth filtration inside monoliths porous structure occurs, instead of cake filtration only. The passage of the gas is therefore not occluded, pressure drops are decreased and more active surface is available for particles deposition and catalytic reactions. By loading porous ceramic monoliths with CuFe_2O_4 catalyst at different wt-percentages, positive effects on CO abatement and PM oxidation were demonstrated. At working temperatures higher than 400 °C, 95 % of CO abatement from flue gas was achieved (on 2-h test average). At the same temperature conditions, PM was reduced for more than 92 %. Main constrains for this application can be referred to the still high pressure drops of filters and the high working temperature needed to activate the catalyst. Appropriate geometries, fitting locations inside equipment and new catalytic materials deserve further investigation. The industrial application of these devices will foresee periodic high temperature regeneration of filters (by microwaves induction), according to the maximum pressure drops level admitted. For CO abatement, new catalysts with lower working temperatures are still investigated.

Acknowledgements

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