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Catalytic Wall Flow Filters for Soot Abatement from Biomass Boilers

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In recent years rising costs of fossil fuels and, on the other hand, the availability of economic incentives and the development of advanced equipment solutions has made biomass combustion an attractive and efficient alternative for the production of heat and electricity at different scales of the plant. In fact, biomass is a renewable energy source widely used for energy production but, unfavourably, it is an important source of inhalable fine PM in ambient air as well. Among the different technologies for the abatement of these pollutants, wall flow catalytic filters may represent an efficient solution, since they combine physical filtration processes with catalytic oxidative reactions. The analysed filters, made of Silicon Carbide and loaded with 20%wt of Copper Ferrite ($CuFe_2O_4$), were properly shaped to be tested in the sampling line at the exhaust of a 30 kW pellet boiler located at ENEA research facilities. The paper presents the main experimental results related to the filter regeneration, the critical operative phase in order to provide adequate performance and service life of the filters. In the tests, regeneration, obtained by means of a high-temperature electrical heater wrapped around the filter housing, started when the pressure drop in the filter exceeded 600 Pa (the transition value from depth filtration to cake filtration) and the heater temperature was gradually increased from 180 °C to 500 °C. Tests showed high efficiency in PM reduction of wall-flow catalytic filters, moreover a relation between the beginning of the regeneration and the temperature of the flue gas at the filter outlet, in the range 220 – 280 °C, was found. The results provided useful information for the future researches, which will be focused on a microwave-based regeneration system, since both the matrix and the catalyst have good dielectric properties.

1. Introduction

While the traditional fossil fuels reserves are slowly running out and their cost are rising up, the demand for alternative renewable energy sources like biomass, which currently contributes about 13 % of the world energy supply, is constantly growing (Khan et al., 2009). In many European Countries the development of advanced equipment has made biomass combustion an attractive, efficient and practical energy source (Verma et al., 2009). However, various studies have shown that the combustion of biomass, especially in small scale heating systems, is an important source of inhalable fine PM and other gaseous pollutants in the ambient air; moreover, besides the health effects on population (Lighty et al., 2000) and the environment (Van Loo and Koppejan, 2002), PM influences the reliability and efficiency of heating systems, since it deposits on the internal surfaces of the plants, causing corrosion, fouling and reduction of heat exchange (Tissari et al, 2008). In this work, the performance of silicon carbide (SiC) catalytic wall flow filters for fine PM abatement have been tested directly at the exhaust of a 30 kW pellet boiler. As showed in recent studies the geometry of these filters allows 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

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goal to investigate the behavior of the filters during regeneration, which is a critical phase in order to guarantee adequate performance and operative life of such filters.

2. Materials and methods

2.1 Filters

The catalytic SiC filters were made by using Pirelli Ecotechnology SiC wall-flow monoliths with 150 cpsi, loaded with 20%wt of $CuFe_2O_4$ as catalyst. The filters were suitably shaped (diameter 26, 29 and 30 mm, length 125 and 60 mm), and wrapped in a heat expanding intumescent ceramic-mat (Interam by 3M), in order to be enclosed in the sampling line at the exhaust of the biomass boiler (Figure 1). Preliminary activity tests were carried out investigating the behavior of 20%wt $CuFe_2O_4$ loaded SiC filters.

Figure 1: Filter housing and intumescent ceramic-mat wrapped around the filter.

2.2 Characterization of materials

The catalytic filters were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDAX), and porosimetry tests. Copper ferrite ($CuFe_2O_4$) was prepared starting from iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) and copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$), mixed in a 2:1 molar ratio, and distilled water, continuously stirred at 60 °C. The bare monoliths were previously impregnated in a 1:1 $HF{:}HNO_3$ mixture at about 45 °C, with the aim to increase the initial porosity (Alok, 1995). The impregnations in the acid mixture were made with different durations, and the optimal impregnation time was individuated in 30 minutes. In this way the initial porosity of the filter was increased to about 24 μm. The catalytic filters were prepared by repeated impregnation steps of SiC wall-flow monoliths in the prepared solution, drying at 60 °C and calcination at 1000 °C after each impregnation, in order to achieve an uniform distribution of the active species (Palma et al., 2015) and the load of 20%wt. The prepared powder of $CuFe_2O_4$ was characterized by X-Ray Diffraction (XRD). Results of XRD analysis showed the presence of the typical peaks of $CuFe_2O_4$ in its tetragonal and cubic form (Palma et al., 2012). Preliminary activities also included the characterization of soot particles emitted by the biomass boiler used in the experimental tests.

2.3 Test facility and operating conditions

Activity tests were carried out in ENEA facilities at Saluggia Research Centre. The filters were placed inside a customised stainless steel housing in the derivation column of the exhaust duct of a 30 kW pellets boiler, fuelled with certified wood pellet (according to UNI EN 14961-2). Tests were carried out at steady-state conditions and full-load operation of the boiler, using the following main settings: 6 kg/h pellets consumption, 8%vol. oxygen content in the flue gas at the exhaust (measured with the lambda sensor equipped in the boiler), 42 L/min water flow rate in the boiler, 7.6 NL/min flue gas flow rate inside the filter (except for the filters with length 60 mm, where a flow rate of 6 NL/min was used). The flue gas flow rate inside the filter was calculated in order to approach isokinetic conditions in the suction nozzle inside the exhaust duct, and it was obtained by means of a Zambelli volumetric pump installed downstream the derivation column. At steady-state, the average flue gas temperature measured at the outlet of the boiler was 127°C, while the water temperatures measured at the inlet and the outlet of the boiler were 63°C and 72°C, respectively.

The main species concentration in the flue gas were measured upstream and downstream the filter by means of extractive methods: CO (0 – 10000 ppm) and CO_2 (0 – 20%) were measured by Maihak UNOR and FER ENOX II NDIR instruments, O_2 (0 – 25%) was measured by Maikah OXOR and Siemens paramagnetic analysers, while TOC (0 – 100 mg/Nm^3) upstream the filter was measured by a NIRA FID analyser. Fine PM concentrations were measured by Pegasor Particle Sensor, able to detect particles with size from a few nm to 2.5 μm, in the range of concentration between 1 and 500 mg/m^3 and under different conditions of pressure,

velocity and temperature of the flue gas. The forced draught in the exhaust duct and the pressure drop in the filter were continuously measured by Aplisens piezoelectric transducers. Temperatures of the flue gas and of the cooling water in the boiler were measured by K-type thermocouples. The water flow rate in the boiler was controlled by a Grundfos e-pump and measured by an ASA electromagnetic induction flowmeter. These quantities were transmitted by a National Instruments DAQ system, and were recorded and monitored by a Labview® program specifically implemented for the present test campaign. Regeneration was obtained by a 900 W high temperature (up to 750 °C) ceramic knuckle electrical heater with diameter 42.5 mm and length 110 mm (Figure 2). The heater temperature was measured by a K-type thermocouple and its operation was controlled by a Watlow PID thermal-regulator PM Express, moreover its electrical consumption was measured by an industrial energy meter Vemer mod. Energy 230. In order to qualitatively assess the temperature on the external surface of the electrical heater, a high-resolution Optris IR camera with three programmable temperature levels (-20 – 100 °C, 0 - 250 °C, 150 – 900 °C) was used.
The regeneration strategy, which was set up after preliminary tests, consisted on stepwise temperature increments from 180 °C (operative temperature to prevent condensation in the flue gas) to 500 °C every 5 minutes, and then further 10 minutes at 500 °C, for an overall duration of 30 mins. Preliminary tests demonstrated that either higher temperatures or longer time steps did not significantly affect the pressure drop in the filter. Each filter was tested for at least 10 hours during two consecutive days. Tests started when the flue gas and the water inside the cooling circuit of the pellet boiler reached steady-state conditions.

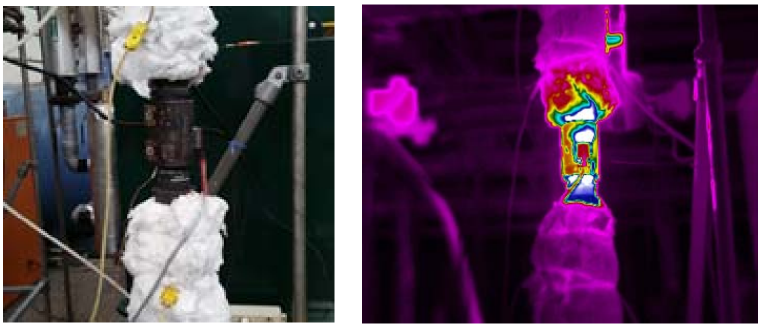

Figure 2: Electrical heater (regenerator, on the left) and IR image at the beginning of regeneration (scale of temperature in the range 20 – 250 °C, on the right).

3. Results and discussions

3.1 SEM-EDAX results

The SEM images were performed by means of SEM mod. LEO 420 V2.04, ASSING, and Energy Dispersive X-ray Spectroscopy (EDX mod. INCA Energy 350, Oxford Instruments, Witney, UK). A SEM image of the soot emitted by the biomass boiler present at the Saluggia Research Centre of ENEA is showed in figure 3.
The SEM image of Figure 3 shows that the soot particles have the typical soot cluster structure with an average size of about 50 nm; furthermore they are characterized by a higher content of heavy metals adsorbed on the carbonaceous matrix. The SEM images (figure 4) also allowed to verify the structure of the catalytic filter, and in particular by means of the EDX analysis were verified the species present on it.

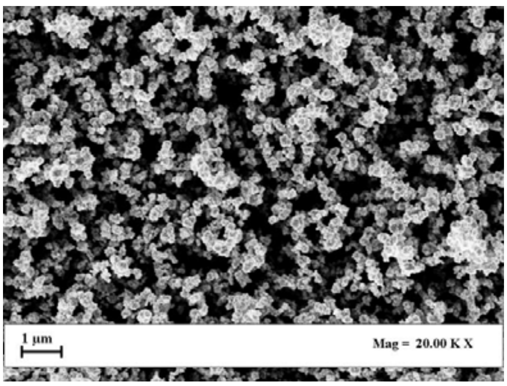

Figure 3: SEM image of soot emitted by the biomass boiler of the Saluggia research centre of ENEA.

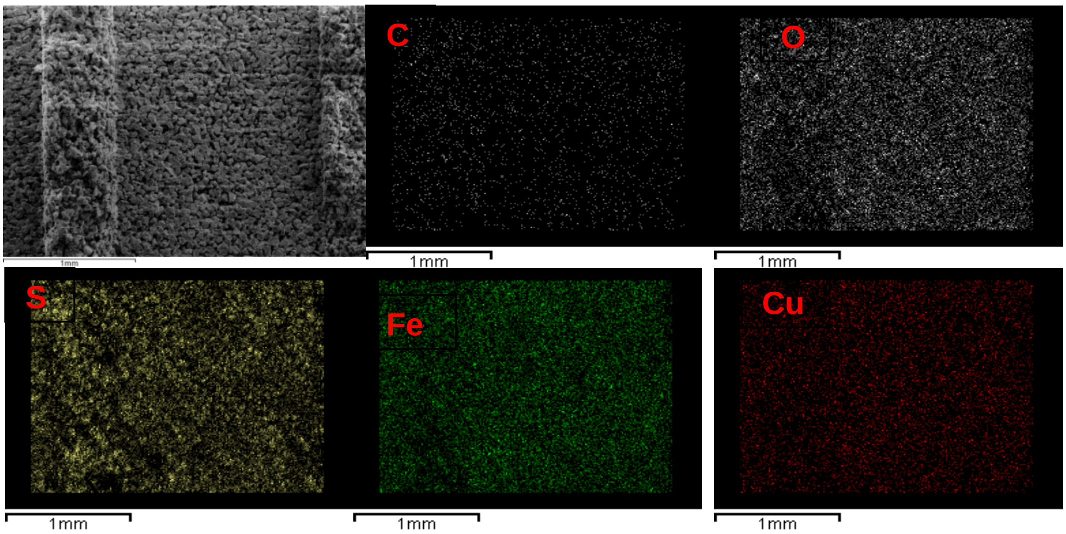

Figure 4: SEM image and distribution of elements, as obtained by EDX element mapping for the 20%wt $CuFe_2O_4$ loaded filter.

The results showed in figure 4 confirmed the very homogeneous distribution of the active species on the filter surface (Stoppiello et al., 2014), and from the images it can be noted that they cover the whole surface of SiC granules. 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. Furthermore the porosimetric analysis evidenced that the pores diameter increased and that they were not occluded, since the median pore diameter decreased from 24 μm to about 17 μm.

3.2 Experimental analysis of the regeneration of the catalytic filters

The typical experimental behaviour of the pressure drops in the filter during regeneration is depicted in Figure 5: after a short (a few minutes) initial phase when Δp rapidly increased, which occurred only in the first cycle, a longer phase followed during which Δp increased slowly and with a linear trend. During this phase the mechanism of depth filtration was dominant and characterised by gradual occlusion of the pores by PM particles. When the pores were partially occluded and the PM particles contributed themselves to filter the upcoming particles in the flue gas, a sharp increase in the Δp occurred and the so-called cake filtration became dominant. The transition from depth filtration to cake filtration occurred generally in the Δp range of 600 - 700 Pa. The electrical heater temperature was increased when Δp permanently exceeded 600 Pa. Tests showed that generally regeneration started when the temperature of flue gas at the filter outlet was in the range 220 – 280 °C (average value around 250 °C), which approached 300 °C with filters of length 60 mm because of the smaller flue gas flow rate. At the beginning of regeneration, Δp was in the range 800 – 1000 Pa, which then rapidly decreased to 500 – 600 Pa, before reaching a stage characterised by a smoother Δp decrease (phases no. 3 and 4, respectively, in Figure 5).

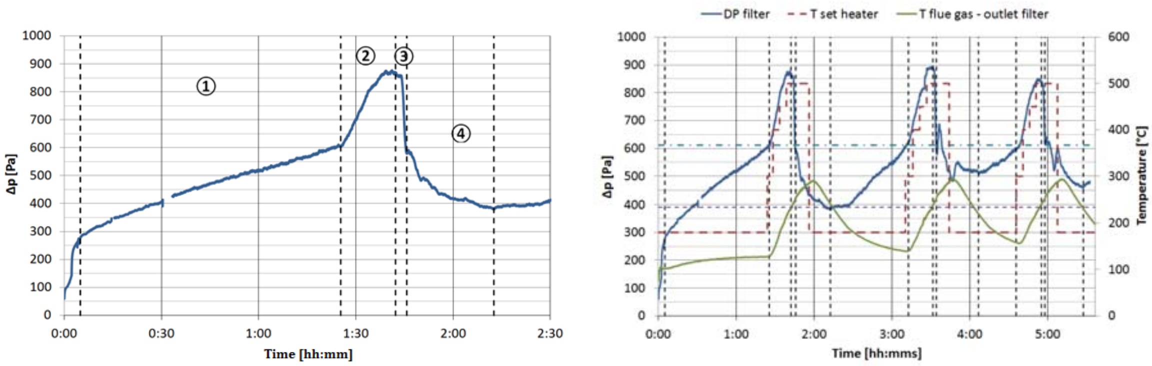

Figure 5: Typical trend of the pressure drop Δp in the filter during regeneration (on the left) and comparison between the Δp in the filter and the flue gas temperature at the outlet of the filter during three cycles (on the right) - filter with porosity of 17 μm and length 125 mm.

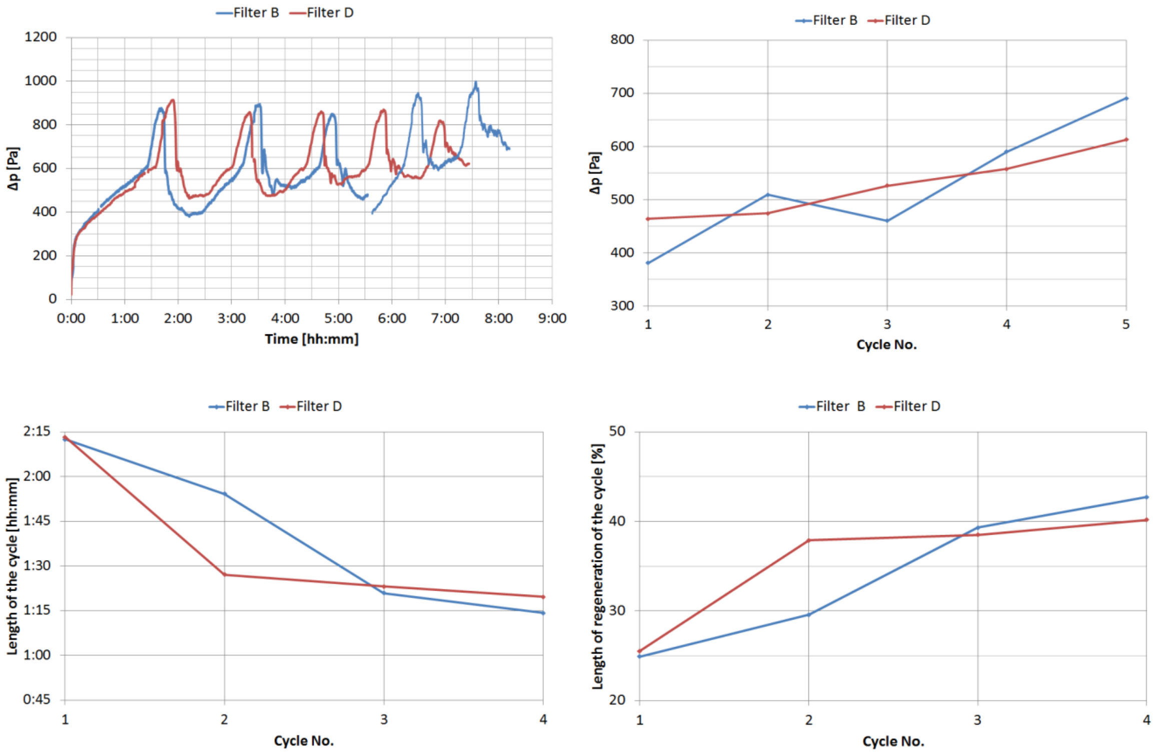

Figure 6: Comparison between two filters with porosity of 17 µm and length 125 mm: pressure drop (top left), Δp at the end of regeneration (top right), length of the cycles (bottom left), and length of the regeneration in each cycle (bottom right).

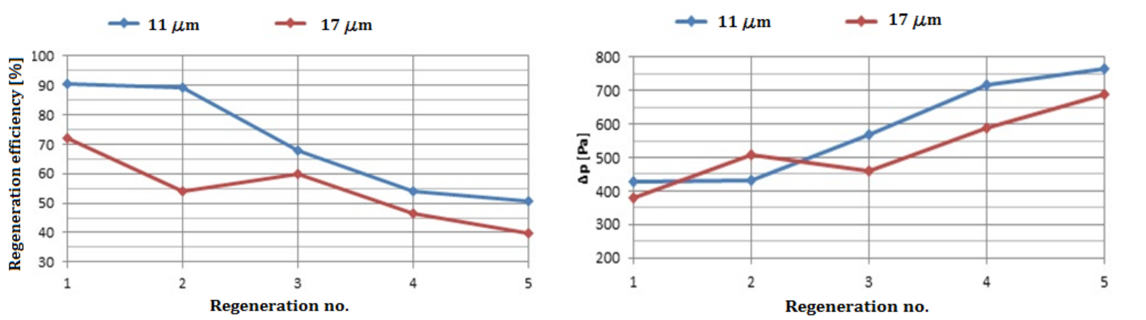

Figure 7: Comparison of the regeneration efficiency (on the left) and pressure drop (on the right) between filters with porosity of 11 µm and 17 µm and length 125 mm.

This effect was partly due to the lower flue gas temperatures, as the electrical heater was set back to 180 °C, which involved lower velocities in the filter and consequently lower pressure drop. The electrical consumption of the heater was equal to 0.3 kWh during regeneration, corresponding to an equivalent specific consumption per unit of volume of the filter equal to 4.5 kWh/dm^3. Furthermore, tests on filters with length 60 mm showed the dependence of regeneration with the flue gas flow rate: with a flow rate of 7.6 NL/min, which was used with filters with length 125 mm, regeneration was less effective and pressure drop higher than with a flow rate of 6 NL/min. The result may proof that shorter filters do not lead to positive effects on the pressure drop during operation and above all during regeneration. The comparison of filters with the same characteristics (i.e. $CuFe_2O_4$ 20 %wt., matrix porosity 17 µm, length 125 mm) showed similar results and a satisfying repeatability for both temperatures and Δp. In both cases the transition between depth and cake filtration occurred at Δp around 600 Pa, and the main differences in the Δp profile were mainly due to the different duration of the first day of tests (Figure 6). The same figure also shows a comparison of the Δp at the end of the regeneration, the duration of the cycles, and the duration of the regeneration in each cycle of the two filters with the same characteristics.

The regeneration efficiency in the present study is the ratio between the initial stabilized Δp (after the rapid increase which occurs in the very first minutes of test, i.e. beginning of phase 1 in Figure 5) and the minimum Δp at the end of each regeneration. Tests demonstrated that regeneration efficiency reduced with cycles, above all after the third cycle, and the duration of the cycles decreased from almost 3 hr to 1 hr after the 5th cycle. After 5 cycles regeneration became too frequent and ineffective, with pressure drops higher than 1000 Pa. As for matrix porosity, filters with average pore size of 17 μm generally had lower values of Δp after regeneration than filters with pore size of 11 μm. On the other side, the regeneration efficiency was higher in the latter filters, approaching 90% after the first cycle instead of 70% in filters with pore size of 17 μm. In both cases, regeneration efficiency dropped to 50% after 5 cycles (Figure 7).

4. Conclusions

Tests have confirmed the high PM abatement efficiency of catalytic wall flow filters, up to 90%, assessed in previous studies (Stoppiello et al., 2014). The present work was focused on regeneration, which is a critical phase in order to guarantee proper performance and adequate service life of the filters. Experimental results have shown acceptable repeatability of the results under the same test conditions. In particular, transition between depth filtration and cake filtration occurred with a pressure drop Δp of about 600 Pa and a flue gas temperature at the outlet of the filter in the range 220 – 280 °C. The maximum number of cycles before the out of service of the filters was generally limited to 5 cycles, and the regeneration frequency increased with the cycles, which resulted in a reduction of their duration from 3 hours to less than 1 hr. Further studies are currently carried out in order to optimize the design of the filters for the PM emissions produced by biomass boilers, in order to increase the service life and to reduce the energy consumption required during regeneration.

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