

## Optimal $\text{CuFe}_2\text{O}_4$ Load for MW Susceptible Catalysed DPF

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In the automotive market, the diesel engines are attractive for their higher fuel efficiency, reliability, and high torque, but they are one of the major sources of Particulate Matter (PM) and Nitrous Oxides (NOx) in the urban area, pollutants associated to environmental and health issues. Thanks to the continuous fundamental and applied research on diesel engine improvement, good results in terms of PM reductions were achieved by combustion system re-design, engine layout modification and the use of more efficient after treatment devices. The Diesel Particulate Filter (DPF) is one of the most important technology to fulfill the strict PM regulations, consisting in alternately plugged parallel square channels, so that the exhaust gases are forced to flow through the porous inner walls: in this way the particles are collected on the surface and in the porosity of the channel walls, progressively blocking the pores. Since the pressure drop increases by the formation of a soot cake as the PM is accumulated, the DPF needs to be periodically regenerated by burning off the accumulated soot. Therefore, DPF is mainly demanded three performances: filtration, pressure drop, and regeneration. In our previous works we showed that the simultaneous use of a MW applicator and a specifically 15 %wt of  $\text{CuFe}_2\text{O}_4$  catalysed DPF, allows to reduce the temperature, the energy and the time required for the filter regeneration. Starting by these very promising results, the objectives of this work are to optimize the catalyst load on the DPF, in order to simultaneously further reduce the PM oxidation temperature and keep low the pressure drop and verify the feasibility of the MW heating technology by comparing the energy balance of the entire process to the actually employed regeneration technologies.

### 1. Introduction

The increasing concern on atmospheric pollution derived from road transportation has led to the introduction of newer and each time more stringent regulation over the past decades. Diesel engines operate under lean conditions, contributing to better fuel economy and lower  $\text{CO}_2$  emissions, whereas controlled combustion temperature results in lower gaseous CO and HCs concentrations in the exhaust (Galvez et al., 2012). Therefore, and due also to their excellent durability, the demand for light-duty diesel vehicles has increased notably in the last years, this trend being expected to continue in the near term future (Beatrice et al., 2012). Engine modifications, such as common rail technology or exhaust gas recirculation (EGR) cooling technology, have helped to lower the emission of particulates and other pollutants in diesel engines conforming the existing legislative demand. Still, there is always a trade-off between the reduction of particulate matter emission and nitrogen oxides (NOx) control.

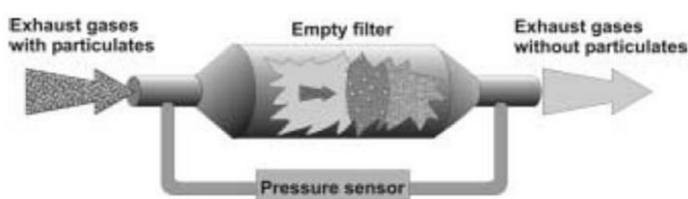


Figure 1: Wall Flow Diesel Particulate Filter

Thus, the use of after-treatment technologies is required, and more efficient technologies are being hunted in order to meet the emission standards (Tsuneyoshi et al., 2012): so a Diesel Particulate Filter (DPF) has to be installed in the exhaust system in most vehicles. Several types of filters have been described in the literature, but the wall-flow monolith is by far the most studied and commercially applied particulate trap (Jansma et al., 2012). It consists of a ceramic structure with alternately plugged parallel square channels (Figure 1). As a consequence, the exhaust gases are forced to flow through the porous channel walls that act as filters; in this way high particulate trapping efficiency (>95 %) can be achieved, as reported in our previous work (Palma et al., 2011).

However, in order to prevent clogging of the filter, the collected soot inside the trap has to be periodically oxidized to regenerate the DPF. The oxidation step is promoted by the so-called 'passive' (at temperatures upstream the DPF of ca. 200 – 400 °C) and 'active' regeneration (temperatures upstream the DPF of ca. 550 – 600 °C) (Liati et al., 2012). The exothermic PM combustion leads in some cases to excessive temperature rise, which may damage the ceramic DPF. The development of a cost effective, fast and safe regeneration procedure is the major remaining technological challenge in the use of this device (Chen et al., 2011): so it is interesting the use of MW energy due to the rapid and selective heating of material through differential MW absorption (Meredith et al., 1998). The results of our previous deposition and on-line regeneration tests on uncatalysed and Copper-Ferrite catalysed DPF, showed that the simultaneous use of the MW and the catalysed filter at lower gas flow rate, allows to reduce the energy supplied and the regeneration time than that required for the uncatalysed filter (Palma et al., 2011). Considering that in terms of durability and MW absorption properties, the residual presence of copper and iron oxides show poor performance, in this work we propose to increase the ferrite load and minimize the presence of copper and iron oxides, in order to simultaneously improve the MW dissipation efficiency and the final catalytic DPF performances. So the objectives of our work are to optimize the preparation procedure of the catalytic DPF in order to maximize the load of  $\text{CuFe}_2\text{O}_4$  on the filter in agreement with a sustainable pressure drop, and to verify the feasibility of this technology by assessing the energy balance of the process, in order to compare it to the actually employed regeneration technologies.

## 2. Results and discussion

In this work  $\text{CuFe}_2\text{O}_4$  catalysed DPFs with different %wt of active species are prepared; the prepared powder of  $\text{CuFe}_2\text{O}_4$  is characterized by X-Ray Diffraction (XRD) and TG-DTA analysis, while the catalysed DPFs are characterized by Scanning Electron Microscopy (SEM), Energy dispersive spectroscopy (EDAX), Hg porosimetry tests, TG-DTA analysis,  $\text{H}_2$ -TPR measurements and bending strength tests.

### 2.1 Catalyst preparation

Differently from the previous preparation procedure (Palma et al., 2011), we changed the drying step (by lowering the temperature value to 60 °C and increasing the duration time to about 30 h) and the calcination step (abrupt heating to 1,000 °C, slow cooling to 500 °C and then quenching to room temperature), since that in the conditions previously developed and optimized for the lower catalyst load, we observed that at higher catalyst load the pores occlusion occurs, together with the occurrence of filter fractures which compromised its use, as also shown in literature (Blissett et al., 1997). With this new procedure, we realized a more uniform and homogeneous distribution of the active species on the DPF walls and inside the porosity, reducing the occlusion of the inner walls pores, allowing to increase the catalyst load up to 30 %wt. Furthermore, XRD analysis showed the presence in our prepared Copper Ferrite of the typical peaks of  $\text{CuFe}_2\text{O}_4$  in its tetragonal and cubic form (Palma et al., 2012).

### 2.2 SEM-EDAX results

Catalysed and uncatalysed samples have been investigated by Scanning Electron Microscopy (SEM), using a Scanning Electron Microscope (SEM mod. LEO 420 V2.04, ASSING), and Energy Dispersive X-ray Spectroscopy (EDX), performed in an Energy Dispersive X-Ray analyzer (EDX mod. INCA Energy 350, Oxford Instruments, Witney, UK): the results reported in our previous works (Palma et al., 2012) showed the very homogeneous distribution of the active species on the filter surface, and the comparison among the uncatalysed filter and the catalysed filter with various  $\text{CuFe}_2\text{O}_4$  loads showed that the active species cover all the SiC granules surface and that increasing their load, they don't deposit inside the inner wall pores but only on the external surface, and so on another layer of Copper Ferrite: in this way there is only the decrease of the pore diameter, but not their occlusion, so allowing its use as catalytic filter. In Figures 2 and 3 are reported the SEM images and the elements distribution as obtained by EDX element mapping, for the uncatalytic and for the 15 %wt catalysed filter, respectively: while on the uncatalytic filter the encountered elements are only C, O and Si (the structural elements of the filter), on the catalytic filter the encountered elements are also Cu and Fe, the catalyst active species: these results confirm that with our

catalytic filter preparation procedure, we can obtain the deposition of the active species on the support without any washcoat.

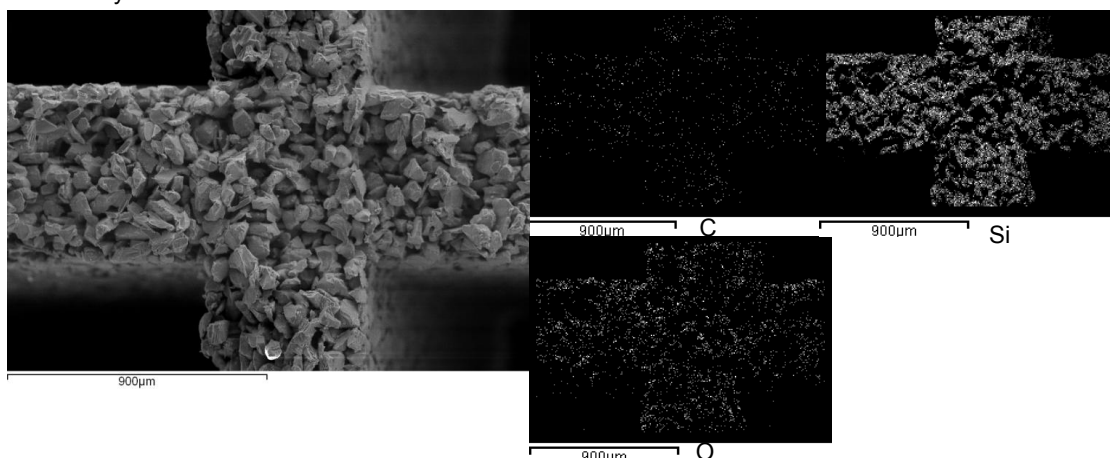


Figure 2: SEM image and distribution of elements, as obtained by EDX element mapping, for the uncatalytic filter

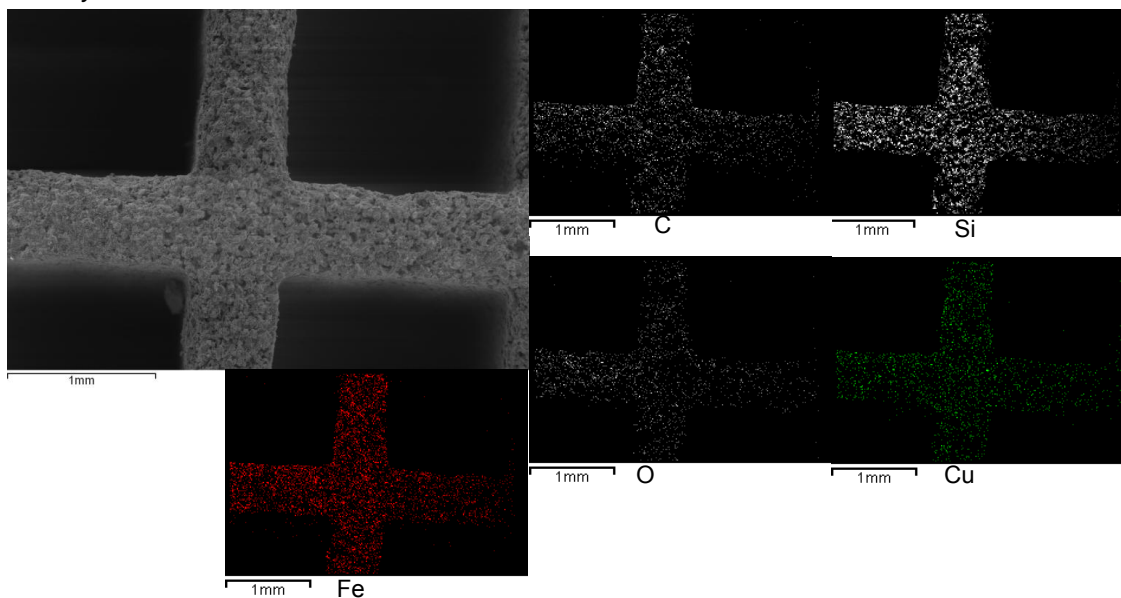


Figure 3: SEM image and distribution of elements, as obtained by EDX element mapping, for the 15%wt  $\text{CuFe}_2\text{O}_4$  catalysed filter

### 2.3 Hg porosimetry tests

The porosimetric characteristics of the filters have been measured by the Hg penetration technique using the “PASCAL 140” and “PASCAL 240” Thermo Finnigan instruments: the results are reported in Table 1.

Table 1: porosimetric characteristics of the catalysed and uncatalysed filters

	Medium pore diameter ( $\mu\text{m}$ )	Total pore volume ( $\text{mm}^3/\text{g}$ )
Uncatalytic SiC DPF	17.0	329
Catalytic DPF with 15%wt of $\text{CuFe}_2\text{O}_4$	14.7	264
Catalytic DPF with 20%wt of $\text{CuFe}_2\text{O}_4$	13.3	247
Catalytic DPF with 25%wt of $\text{CuFe}_2\text{O}_4$	12.3	143
Catalytic DPF with 30%wt of $\text{CuFe}_2\text{O}_4$	12.0	134

From these data, it is evident that the increase of  $\text{CuFe}_2\text{O}_4$  load results in the medium pores diameter and total pore volume decrease. In particular, the main changes of these values are observed up to 20 %wt of active species, while the further increase from 20 % to 30 %wt gives only little decreases. These results can be likely due to the behavior deposition of the catalyst that occurs inside the pores and on the walls of the DPF at the lower load, while only on the external surface at the higher catalyst load.

#### 2.4 TG-DTA analysis

The catalytic activity of powder catalyst and catalyzed DPF, was evaluated by simultaneous TG-DTA analysis (SDT Q600 TA Instruments) of soot alone and of soot mixed in a mortar with milled catalyzed DPF samples at different catalyst load and with the powder catalyst. Samples were heated in air (flow rate =  $100 \text{ Ncm}^3 \text{ min}^{-1}$ ) from 293 to 973 K with a heating rate of  $10 \text{ K min}^{-1}$ . The results are reported in Figure 4, as Derivative Weight (in %/min), referred to the total amount of soot in the sample, in function of Temperature. The TG curve of soot alone shows its typical behaviour (ignition temperature of about  $550 \text{ }^\circ\text{C}$  and maximum reaction rate at about  $620 \text{ }^\circ\text{C}$ ). The results relevant to the TG of soot mixed with the  $\text{CuFe}_2\text{O}_4$  powder show that the ignition temperature is lowered to  $380 \text{ }^\circ\text{C}$  and the maximum combustion rate temperature is lowered to about  $450 \text{ }^\circ\text{C}$ , confirming its very good soot oxidation activity. The comparison of the results relevant to the soot mixed with  $\text{CuFe}_2\text{O}_4$  catalyzed DPF at different catalyst load, show that increasing the load of active species on the filter the ignition temperature and the maximum combustion rate temperature are both lowered and, more important, the rate of the catalytic combustion reaction increases.

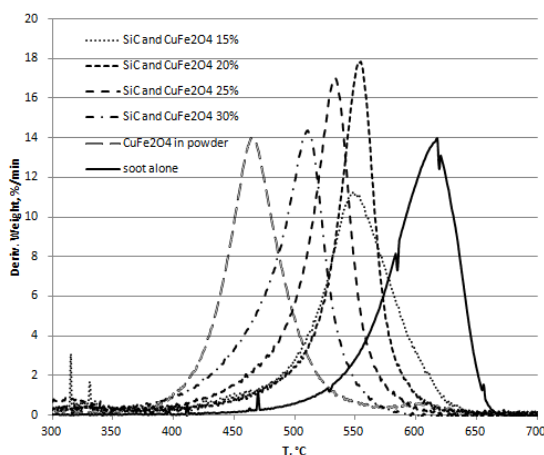


Figure 4: TG test performed on soot alone, soot and  $\text{CuFe}_2\text{O}_4$ , soot and SiC DPF with 15 %wt, 20 %wt, 25 %wt and 30 %wt of  $\text{CuFe}_2\text{O}_4$

#### 2.5 $\text{H}_2$ TPR Analysis

The  $\text{H}_2$ -TPR analysis was carried out using a SiC monolith catalysed with 15%wt of  $\text{CuFe}_2\text{O}_4$  from room temperature to  $900 \text{ }^\circ\text{C}$  at a heating rate of  $5 \text{ }^\circ\text{C/min}$  in 5 %  $\text{H}_2/\text{N}_2$  flow. The reaction parameters (temperature and concentrations) have been monitored by the mean of an HIDEN Analytical system, including a mass spectrometer.

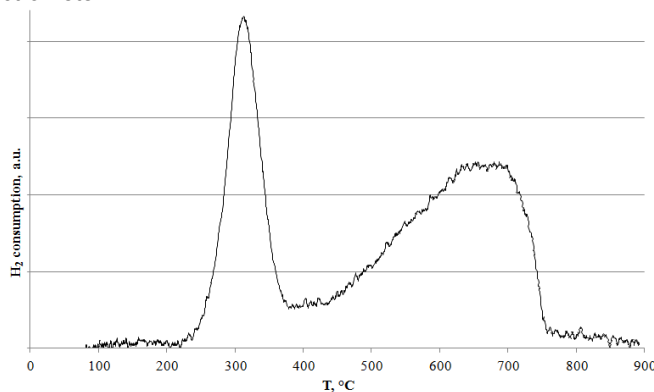


Figure 5:  $\text{H}_2$ -TPR profile of a SiC monolith catalysed with 15 %wt of  $\text{CuFe}_2\text{O}_4$

Figure 5 shows the H<sub>2</sub>-TPR profile: two pronounced reduction peaks were observed at about 300 °C and 610 °C; these peaks are attributed to the reduction of CuFe<sub>2</sub>O<sub>4</sub> to Cu and Fe<sub>3</sub>O<sub>4</sub>, and subsequently of Fe<sub>3</sub>O<sub>4</sub> to Fe (Kameoka et al., 2010). The total amount of H<sub>2</sub> consumed for Cu mole (H<sub>2</sub>/Cu ratio) was 4.4, which is consistent with that for the complete reduction of CuFe<sub>2</sub>O<sub>4</sub> to Cu and Fe.

The overall reaction is:



The value of 4.4 corresponds to about 17 %wt of CuFe<sub>2</sub>O<sub>4</sub>, that is in a quite good agreement with the estimated 15 %wt of CuFe<sub>2</sub>O<sub>4</sub> on the monolith. As shown in literature (Kameoka et al., 2005), after the reduction, mixture of Cu and Fe is favorable for the formation of CuFe<sub>2</sub>O<sub>4</sub> at about 800 °C in air, even if not all in the same crystalline form. So we can say that through redox process, the CuFe<sub>2</sub>O<sub>4</sub> completely reduces to Cu and Fe and then returns to CuFe<sub>2</sub>O<sub>4</sub> confirming that it is a very good oxidation catalyst.

## 2.6 Bending strength tests

The results of the bending strength tests performed in the Pirelli Ecotechnology laboratory on the catalysed and uncatalysed SiC samples show that the increase in the catalyst load results in a higher DPF bending strength (respectively 30 MPa, 50 MPa and 52 MPa for the uncatalysed, 15 %wt of CuFe<sub>2</sub>O<sub>4</sub> and 30 %wt of CuFe<sub>2</sub>O<sub>4</sub> catalysed DPFs). We can observe that the main gain is observed up to 15 %wt of CuFe<sub>2</sub>O<sub>4</sub>, while the further increase to 30 % gives an almost unappreciable rise. These results confirm our assumptions on the catalyst deposition behaviour.

## 2.7 Catalytic activity tests

In Figure 6 are reported the ΔP and the outlet gas temperature as function of time during the regeneration phase of two catalytic DPFs, with 15 % and 20 %wt load of active species. In all the tests, as showed in our previous works (Palma et al., 2011), we heat the DPF with a lower gas flow rate (30 L/min), with the MW generator set at 50 % of its maximum power, and the DPF average filtration efficiency is about 99.5 %. As evident from the Figure 6, simultaneously to the MW application, the outlet gas temperature and the slope of ΔP-time curve increase.

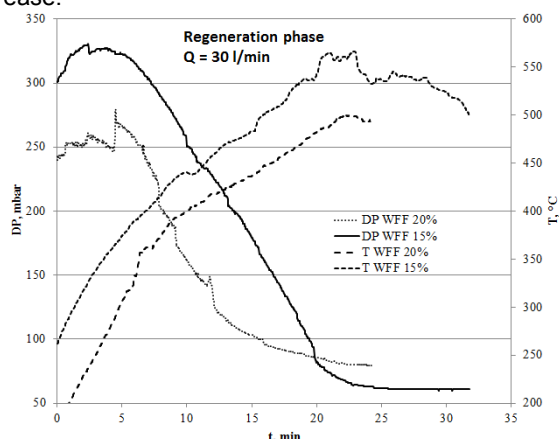


Figure 6: DP and temperature profiles during the regeneration phase

Table 2: Comparison of the energy required in DPF regeneration

Regeneration technology	Regeneration Energy required (kJ)/ DPF L
MW assisted regeneration of 15 % CuFe <sub>2</sub> O <sub>4</sub> catalysed SiC DPF	5,700
MW assisted regeneration of 20 % CuFe <sub>2</sub> O <sub>4</sub> catalysed SiC DPF	3,300
Fuel post-injections (Parks et al., 2012)	14,640
Electrically Assisted DPF regeneration (Parks et al., 2012)	3,643

By looking more deeply, it is possible to emphasize that the increase in the catalyst load results in higher initial DP across the filter, in a lower maximum combustion temperature (350 °C vs 400 °C) and in a faster regeneration phase. By comparing the energy required in MW assisted catalytic DPF regeneration and in the actually employed regeneration technologies, summarized in Table 2 as Regeneration Energy required (kJ) for DPF L, performed with a soot load on the filter of about 5 g/L, we can observe that the simultaneous use of the MW technology and the 20 % CuFe<sub>2</sub>O<sub>4</sub> catalysed DPF allows an energy saving of

about 77 % with respect to the fuel post-injections and of about 10 % with respect to an electrically assisted DPF regeneration (Parks et al., 2012).

## Conclusions

The new preparation procedure (drying step at a lower temperature, 60 °C instead of 120 °C, and for a longer time, and different calcination step) assures a more homogeneous distribution of the active species on the DPF so avoiding the occlusion of the inner walls pores and the filter fractures, and the formation of the CuFe<sub>2</sub>O<sub>4</sub> in the desired form (as confirmed by XRD analysis). The analysis performed on the DPFs showed that the increase in the load of active species up to 30 %wt resulted in lower soot oxidation temperature and increased reaction rate, decrease of the medium pore diameter and total pore volume, higher bending strength. The H<sub>2</sub>-TPR measurements showed two pronounced reduction peaks attributed to the reduction of CuFe<sub>2</sub>O<sub>4</sub> to Cu and Fe<sub>3</sub>O<sub>4</sub>, and subsequently of Fe<sub>3</sub>O<sub>4</sub> to Fe. As shown in literature, after the reduction, mixture of Cu and Fe is favorable for the formation of CuFe<sub>2</sub>O<sub>4</sub> at high temperature (about 800 °C in air), even if not all in the same crystalline form. So we can say that through redox process, the phase transition from CuFe<sub>2</sub>O<sub>4</sub> to Cu and Fe<sub>3</sub>O<sub>4</sub>, and to Cu and Fe and finally return to CuFe<sub>2</sub>O<sub>4</sub> implying that CuFe<sub>2</sub>O<sub>4</sub> is a very good oxidation catalyst. The deposition and on-line regeneration tests performed using a catalytic DPF with 15 % and 20 %wt catalyst load showed that the increase in the active species load resulted in higher initial pressure drops across the filter, in a lower maximum combustion temperature and in a faster regeneration phase, so confirming the TG-DTA results, and, more important, in a higher energy saving. The comparison of the energy required in MW assisted catalytic DPF regeneration and in the actually employed regeneration technologies, shows that the simultaneous use of the MW technology and the CuFe<sub>2</sub>O<sub>4</sub> catalysed DPF allows an energy saving of about 77 % with respect to the fuel post-injections and of about 10 % with respect to an electrically assisted DPF regeneration. These data confirm the palatability of the MW technology in the DPF regeneration phase.

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