Microwave susceptible catalytic filters for diesel soot abatement

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Introduction

NOx reduction up to 80%

PM reduction up to 60%

<table>
<thead>
<tr>
<th>Year</th>
<th>EURO 1</th>
<th>EURO 2</th>
<th>EURO 3</th>
<th>EURO 4</th>
<th>EURO 5</th>
<th>EURO 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1993</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2014</td>
<td></td>
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</table>

NOx+HC

PM
**Particulate Matter effects**

**Effects on human health:**
- diseases of respiratory and cardio-circulatory systems
- Increase in cancers

**Effects on environment:**
- disturbances in the propagation and absorption of solar radiation
- reduction in atmospheric visibility
Introduction

The most applied route to reduce particulate emissions under EU standards is the use of the Wall-Flow Diesel Particulate Filters (DPFs). They consist of ceramic monoliths with alternately plugged channels: so the exhaust gas is forced through the wall and the soot is collected on the surface and inside the porosity of the channels walls.

Exhaust flow and particulate  
Porous wall of the channel  
Cake filtration of the particulate
Wall Flow Filtration Mechanism

- Depth filtration
- Diffusional deposition
- Inertial deposition
- Streamline interception

Cake filtration

When the accumulated soot reaches a critical level, DPF must be regenerated to maintain efficient engine operation.
DPF Regeneration... Drawbacks

- High temperatures (> 600°C) are required for filter regeneration
- The combustion often generates moving high temperature waves, the temperature of which may exceed in some cases the melting temperature of the filter
- Also for a catalyzed DPF the temperature necessary for soot removal is higher than the average exhaust gas temperature

It must be added energy!!

Currently the regeneration process is performed by post-injection and “fuel-born” catalysts resulting in ....

- *complex engine management cycle*
  - *higher fuel penalty*

Hence, in addition to the post-injection further active method of regeneration are under investigation.
Innovative catalytic DPF regeneration technology

- Catalyst: CuFe$_2$O$_4$

- Microwave assisted regeneration: selective and instantaneous heating, function only of the dielectric properties of the materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Dielectric constant $\varepsilon'$</th>
<th>Dielectric loss factor $\varepsilon''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel soot</td>
<td>10.700</td>
<td>3.600</td>
</tr>
<tr>
<td>Quarzo</td>
<td>3.800</td>
<td>0.001</td>
</tr>
<tr>
<td>Cordierite</td>
<td>2.900</td>
<td>0.140</td>
</tr>
<tr>
<td>Alumina ceramic Al$_2$O$_3$</td>
<td>8.900</td>
<td>0.009</td>
</tr>
<tr>
<td>SiC</td>
<td>30.000</td>
<td>11.000</td>
</tr>
</tbody>
</table>
Objectives

To Prepare and characterize a specifically MW sensible catalytic SiC-WFF, loaded with Copper-Ferrite

To perform On-line soot deposition and regeneration tests to demonstrate the use of microwave heating for DPF regeneration

To Compare the energy required for the regeneration of the catalytic filters
Materials

Commercial SiC Wall Flow Filters with 150 cpsi by Pirelli EcoTechnology

<table>
<thead>
<tr>
<th>Total channels</th>
<th>Open channels</th>
<th>Channel length (L)</th>
<th>Filter wall thickness</th>
<th>a [mm]</th>
<th>b [mm]</th>
<th>c [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>585</td>
<td>277</td>
<td>1.5</td>
<td>0.6</td>
<td>36</td>
<td>80</td>
<td>124</td>
</tr>
</tbody>
</table>

Engine

(Lombardini LDW 502)

The engine used is a 505 cm³ bi-cilindrical city car water cooled diesel engine with 7kW@3600 r.p.m.
Materials and Engine Characterization by Hg porosimetry test on WFF...

Opacity, soot concentration and filtration efficiency at various operating conditions, for two different engine load

<table>
<thead>
<tr>
<th>Low load</th>
<th>High load</th>
</tr>
</thead>
<tbody>
<tr>
<td>rpm</td>
<td>Opacity in [%]</td>
</tr>
<tr>
<td>600</td>
<td>15.1</td>
</tr>
<tr>
<td>1100</td>
<td>13.2</td>
</tr>
<tr>
<td>1500</td>
<td>10.7</td>
</tr>
<tr>
<td>1900</td>
<td>7.1</td>
</tr>
</tbody>
</table>

- Untreated filter: Total porosity [%], Average pore radius [Å], Weight density [g/cm³], Apparent density [g/cm³]
- Heat-treated filter: Total porosity [%], Average pore radius [Å], Weight density [g/cm³], Apparent density [g/cm³]
Catalyst preparation: wet impregnation

Sic filters were catalysed by:

- **Impregnation**: 60°C - 30 min
- **Drying**: 60°C - 9 h
- **Calcination**: 1000°C - 30 min

The final value of the active species on the WFF is up to 30%wt.
The TG curve of soot alone shows very low reactivity, with the ignition temperatures of about 550°C and the maximum of reaction rate at about 620°C. The TG curves of soot and SiC-CuFe$_2$O$_4$ mix show that, by increasing the load of active species, the ignition temperature and the temperature of maximum combustion rate ($T_m$) are lowered, as well as the combustion reaction rate is increased.
XRD analysis shows the typical peaks of CuFe$_2$O$_4$ in the tetragonal and cubic form, and the presence of two other peaks, corresponding to CuO and Fe$_2$O$_3$. 
TPR analysis

Two pronounced reduction peaks at about 300°C and 610°C, due to the reduction of CuFe$_2$O$_4$ to Cu and Fe$_3$O$_4$, and, subsequently, the reduction of Fe$_3$O$_4$ to Fe.

The consumed H$_2$ corresponds to about 17%wt of CuFe$_2$O$_4$, which is in a quite good agreement with the estimated 15%wt of CuFe$_2$O$_4$ on the monolith
Active species adhesion test

- Very low weight losses
- The active species were deposited on the monolith without any washcoat

Ultrasonic bath
Cycle time: 5 min
SEM images
- Homogenous distribution and good adhesion of the active species on the SiC granules
  - Tight contact between the active species and the SiC granules
  - Average thickness of the catalyst layer is of about 3 micrometers
The elements which are evidenced by EDX are the ones of the structural material of the filters (C, and Si), as well as the ones of the catalytic active species (Cu and Fe)
**Experimental Plant**

**On-line SOOT deposition and DPF regeneration test**

Regeneration step in two different ways:
- by pre-heating the diesel exhaust stream with the electrical resistances
- by heating the WFF only with the microwave generator (2kW max)
Typical soot loading on a SiC WFF

The average opacity at the DPF inlet: 22% (Csoot : 45 mg/m³)

The average opacity at the DPF outlet: 0.02% (Csoot : 0.04 mg/m³)

Average filtration efficiency higher than 99%

Transient time is lower than 3 min.

Three different stages of soot loading in the DPF:
1. the soot starts to fill the pores in the WFF
2. the soot layer is forming on the surfaces of the WFF
3. the soot layer reaches an appreciable thickness, and starts to act itself as a filter

From this point, an additional increase in the pressure drop curve slope is observed.
MW assisted regeneration tests for uncatalytic filters

Operating engine conditions:
- Deposition: 600 rpm, High load, flow rate 100 l/min
- Regeneration: 600 rpm, Low load, flow rate 100 l/min
- Starting Soot load: 5g/l

In the range of 200-450°C the temperature increase results in a further pressure drop increase. A sensible decrease in the pressure drop is only observed at outlet temperature higher than 550°C, corresponding MW power higher than 1500W.

The MW power was raised from 1200 W to 1800 W to obtain the filter regeneration.

After about 70 minutes the regeneration phase is not yet completed.
MW assisted regeneration tests for 15%wt catalytic filter

operating engine conditions:
- deposition: 600 rpm, High load, flow rate 100 l/min
- regeneration: 600 rpm, Low load, flow rate 100 l/min
- Starting Soot load: 5g/l

A similar pressure drop behaviour as function of time is obtained for the catalytic filter but...

1. the regeneration starts at lower temperatures
2. the MW power required to ignite the system is lowered
3. at the same MW power value the regeneration rate is very higher

The complete filter regeneration is obtained in about 30 min.
The influence of the gas flow rate on the MW assisted regeneration tests for catalytic WFF:

Operating engine conditions:
- Deposition: 600 rpm, High load, flow rate 100 l/min
- Regeneration: 600 rpm, Low load, flow rate 30 l/min
- Starting Soot load: 5g/l

Reducing the gas flow rate from 100 to 30 l/min:
1. MW power required to ignite the system is further lowered
2. Similar regeneration behavior obtained with only about 900W instead of 1800.

Reduced quenching effect of the cold gas flow through the filter.

Very fast regeneration: all the regeneration phase lasts about 20 minutes.
MW assisted regeneration phase

- For the uncatalysed case the regeneration starts for MW power higher than 1500 W. After about 1h the regeneration is not yet completed.
- The 15%wt catalyst load allows simultaneously to regenerate at lowered MW power and higher reaction rate giving the complete soot removal in about half time.
- At lower gas flow rate the MW energy is used mainly for the soot combustion allowing an higher energy saving and a regeneration time further reduced.
Regeneration phase: exhaust gas analysis

Very good oxygen balances verified

Very high selectivity to $\text{CO}_2$ likely due to the lowered temperature and to the catalyst presence.
Regeneration phase: effect of catalyst load

- **On set temperature:** 380 °C
- **Regeneration time:** 25 min

- **On set temperature:** 320 °C
- **Regeneration time:** 20 min

- **On set temperature:** 300 °C
- **Regeneration time:** 15 min
Energy comparison

By integrating the instantaneous MW power as function of time one can obtain the overall energy applied for the regeneration phase.

<table>
<thead>
<tr>
<th>Fuel post-injection</th>
<th>7400 kJ/DPF liters</th>
</tr>
</thead>
<tbody>
<tr>
<td>15% wt loaded DPF</td>
<td>5700 kJ/DPF liters</td>
</tr>
<tr>
<td>20% wt loaded DPF</td>
<td>3300 kJ/DPF liters</td>
</tr>
<tr>
<td>30% wt loaded DPF</td>
<td>2300 kJ/DPF liters</td>
</tr>
</tbody>
</table>
Deposition phase: effect of catalyst load

- Higher initial pressure drop at the increase of the catalyst load
- Same trend during the deposition phase
## Textural properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area (m²/gr)</th>
<th>Average pore diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder of CuFe₂O₄</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Bare SiC monolith</td>
<td>0.3</td>
<td>17</td>
</tr>
<tr>
<td>Catalytic DPF with 15%wt of CuFe₂O₄</td>
<td>0.5</td>
<td>15</td>
</tr>
<tr>
<td>Catalytic DPF with 20%wt of CuFe₂O₄</td>
<td>0.9</td>
<td>13</td>
</tr>
<tr>
<td>Catalytic DPF with 30%wt of CuFe₂O₄</td>
<td>0.9</td>
<td>12</td>
</tr>
</tbody>
</table>

- The increase in the catalyst load results in the increase of the specific surface area and in the decrease of the average pore diameter.
SEM images
## Porosimetric tests

<table>
<thead>
<tr>
<th>Uncatalytic monolith Duration of acid treatment [min]</th>
<th>Pores average diameter [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>17.0</td>
</tr>
<tr>
<td>2</td>
<td>18.0</td>
</tr>
<tr>
<td>4</td>
<td>19.0</td>
</tr>
<tr>
<td>6</td>
<td>20.0</td>
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<td>8</td>
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<td>10</td>
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<td>20</td>
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<tr>
<td>30</td>
<td>24.0</td>
</tr>
<tr>
<td>35</td>
<td>24.5</td>
</tr>
</tbody>
</table>

WE DEVELOPED A DEDICATED CHEMICAL TREATEMENT TO REALIZE THE ACIDIC CARRIER LEACHING AND OBTAIN A CONTROLLED EROSION TO MODIFY THE INITIAL AVERAGE PORES DIAMETER

<table>
<thead>
<tr>
<th>20% wt CuFe$_2$O$_4$ loaded SiC monolith</th>
<th>Pores average diameter [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>No acid treatment</td>
<td>13</td>
</tr>
<tr>
<td>After 30 min of acid treatment</td>
<td>17</td>
</tr>
</tbody>
</table>
Catalytic Filters with modified porosity

- Increased duration of the deposition phase
- Decrease of the frequency of DPF regeneration phases
Conclusions

- MW sensible catalytic Wall Flow Filters were prepared by depositing Copper Ferrite on commercial SiC monoliths (Pirelli Ecotechnology)

- The catalyst allowed to decrease the soot ignition temperature up to about 300 °C.

- Very high filtration efficiency as in the case of the original monolith,

- The designed experimental apparatus allowed us to verify that is possible to achieve the complete filter regeneration employing only microwaves

- The higher catalyst load allowed to decrease the time required for the MW regeneration stage (from 40 min up to 20 min) and lowered the energy needed to regenerate the filter, also with respect to fuel post-injection

- A dedicated chemical treatement to realize the acidic carrier leaching and obtain a controlled erosion to modify the initial average pores diameter Was developed
THANKS FOR YOUR ATTENTION

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