

PLASMA-ASSISTED DIESEL OXIDATION CATALYST: IMPROVEMENT OF LIGHT-OFF TEMPERATURE FOR CO AND UNBURNED HYDROCARBONS

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ABSTRACT

Low temperature oxidation of high levels of CO and gas phase hydrocarbons (HCs) emissions, as created by HCCI-like combustion engines, has been investigated. Performances of commercial Euro5 Diesel oxidation catalyst (DOC, Pt-Pd/Al₂O₃) were evaluated by determining its light-off temperature when it is placed downstream of a pilot-scale multi-DBDs reactor powered by an AC generator delivering an average power in the range 50-300 W. DOC performances with and without plasma have been systematically compared under various operating conditions (input energy density, space velocity, flow rate, temperature). Results demonstrate the capability of the plasma to lower the DOC light-off temperature (T_{50}) for CO and HCs. Improvement of T_{50} by about 60°C was obtained and could be explained through chemical exothermic mechanisms involving the plasma species over the active catalytic sites. This approach shows that DOC and plasma work synergistically to promote selectively HCs oxidation at low temperature. C₃H₆ exhibits the high oxidation rate followed by C₇H₈, C₁₀H₂₂, and CH₄.

1. INTRODUCTION

The increasingly stringent environmental regulations on Diesel emissions are exerting pressure on car manufacturers to reduce polluting emissions from exhaust systems. While the diesel oxidation catalyst (DOC) is effective for carbon monoxide (CO) and unburned hydrocarbons (HCs) control at the Diesel exhaust temperature levels, there remain issues of catalyst cost and low temperature activity. It is important to begin the conversion of CO and HCs as soon as possible after engine start (i.e. cold start regime) to reduce harmful emission. In

Diesel application, these requirements are generally achieved by the use of high noble metal loadings and hydrocarbon adsorbers [1].

Among several approaches under development in the last decade, research efforts have been focused on finding a catalyst that can be combined with non-thermal plasma to reduce nitrogen oxide emissions from automotive exhausts gases (lean-burn gasoline and Diesel exhausts) [2-4]. More recently, the conversion of all classes of emissions associated with internal combustion engines (unburned fuel, carbon monoxide, and particulate matters) were considered [5]. In that field, corona and dielectric barrier discharges (DBD) in conjunction with number of materials having catalyst activity for pollutants reduction have been studied extensively.

This study is mainly focused on the gas treatment efficiency together with reducing catalyst activation temperature when a DOC catalyst was connected downstream to DBD reactor in laboratory-scale and bench-scale experiments. The effectiveness of the process with regard to NO_x, CO, HCs removal chemistry and DOC performance evaluation will be discussed.

2. EXPERIMENTAL

Two experimental installations were used for these studies. The first was the GREMI laboratory-scale experimental setup (gas flow rate up to 20 L/min) and the second was the RENAULT synthetic gas test bench facility (gas flow rate up to 260 L/min). The gas feed stream simulating HCCI Diesel exhaust (Homogeneous Charge Compression Ignition) contained a mixture of O₂ (10%), CO₂ (4%), CO (8500 ppm), HCs (1500 ppmC), NO (100 ppm), H₂O (4%), and N₂ as balance was prepared in a gas and liquid

handling system and concentration of each compound was controlled by calibrated high-precision mass flow controllers. HCs are a mixture of 4 hydrocarbons (propene, toluene, decane, methane).

Fig. 1 show the GREMI-Lab experimental arrangement which consists of a continuous flow gas generation and heating systems, plasma and catalytic reactors, and detection systems.

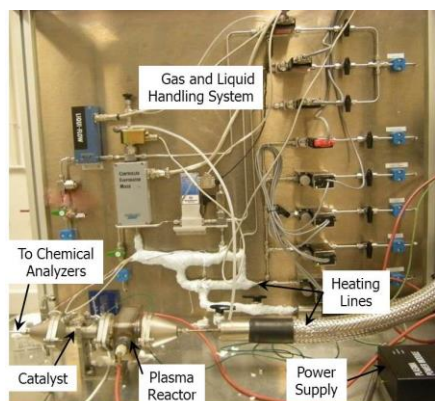


Fig 1: Photography of the GREMI experimental set-up.

The plasma reactor is a multi-DBDs pilot-scale reactor in planar geometry. Each elementary part of the reactor consists of a pair of thin metal electrodes covered by alumina plates separated by a gap of about 1.5 mm. The plasma reactor was powered by a high voltage, high frequency AC generator (11 kV - 15 kHz) delivering a plasma power which can be varied from 50 to 300 W with an energy conversion efficiency of around 75%. The plasma reactor and the power supply device are designed to fit an integrated after-treatment system which can be directly installed on the vehicle exhaust line casing. Fig. 2 shows photography of the plasma reactor operating under nitrogen flow.



Fig 2: Photography the plasma reactor

The electrical energy consumption of the plasma reactor was evaluated through the specific input energy (SIE) which is the energy deposited per unit volume of gas in the discharge reactor (J/L) at standard conditions (25°C and 1 atm). In this work, the specific input energy was in the range 154-1124 J/L for experiments at low flow rate

and in the range 57-85 J/L for experiments at high flow rate. For all experiments, the electrical measurements were made using a Tektronix high voltage P6015A probe (75 MHz 1:1000 ratio) and Pearson 4001 current probe connected to Tektronix DPO 3054 oscilloscope (500 MHz, 2.5 Gs/s).

Commercial Euro5 DOC (honey-comb structure monolith-supported Pt-Pd/Al₂O₃, ratio 2:1) has been tested in these experiments. This sample catalyst was hydrothermally aged for 5 h at 750°C under N₂-O₂- H₂O (10%) mixture.

The exhaust line was equipped with temperature sensors and temperature programmed surface reaction (TPSR) was used to determine CO and HCs light-off curves for plasma, DOC, and plasma assisted DOC systems.

The exhausts gas was analyzed by a Pierburg AMA 2000 system, Nicolet 6700 Ft-IR spectrometer, MRU Vario Plus electrochemical analyzer, and IN USA-IN-2000 ozone analyzer.

3. RESULTS

Various techniques were used to evaluate the oxidation catalysts performances. Measurements of surface composition, area, structure, porosity, acidity, and dispersion of active metals of oxidation catalysts can be related to the catalyst performance. However, one direct measurement of its performance is to determine its light-off temperature, the temperature at which significant oxidation reactions occur (T₅₀ corresponds to temperature at which the conversion rate of gaseous constituents reaches the 50% level). In general, it is true that the lower the light-off temperature, the more effective will be the catalyst performance [7].

A difference between conventional catalytic and plasma activated reactions is that in the latter many active species, free energized electrons, ions, and UV light could be generated at low temperature. Under oxygen-rich conditions, as is the case of Diesel exhaust, the plasma promote oxidation of compounds, some oxidation reactions can produce undesirable products and in fact, be counterproductive to the plasma purpose. On the other hand, intermediate species or "by-products" created by the plasma discharges could be benefit for the catalyst activation especially at low temperature and to prevent the poisoning of its actives sites.

Fig. 3 depicts the CO and HCs conversion by plasma in the absence of downstream DOC at 250 W input plasma power. This data is shown for background information used for comparison with catalyst and plasma-catalyst data. As can be seen in the figure, high hydrocarbons removal efficiency (80%) can be reached by plasma treatment at 230°C. A fraction of the removed hydrocarbons contribute to form carbon dioxide although the measurements were not precise enough to detect such a small change in CO₂ against the 4% of background concentration. Detailed study show that propene exhibit the high oxidation rate followed by toluene, decane, and methane. Analysis of gas composition at outlet of the plasma reactor in laboratory-scale experiments revealed the existence of compounds already reported [11-12]. We should highlight the presence of several non-regulated HC-derived emissions, such as aldehydes (CH₃CHO, CH₂O) as well R-NO_x (CH₃ONO₂, CH₃NO₃), formic acid (CH₂O₂), nitrogen dioxide (NO₂) and some extend of acids (HNO₂, HNO₃).

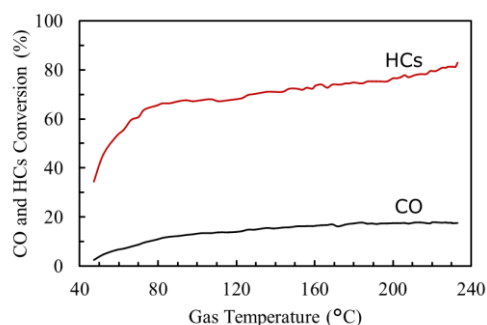


Fig 3: NO and NO₂ Concentrations for DOC and plasma-DOC vs gas temperature for different plasma energy deposition.

For both catalyst-alone and combined plasma-catalyst treatment (catalyst downstream of the plasma reactor), we focus on light-off temperature for CO and hydrocarbons oxidation. Data for CO for both DOC alone and plasma-DOC treatment are shown in Fig. 4 for the same conditions (gas mixture, flow rate, plasma power). When the system is heated, we observe a fast decrease of the CO concentration for both systems. In the case of plasma-DOC treatment, the CO light-off temperature is clearly shifted toward lower temperature compared to thermal-only curve. T₅₀ for CO is about 140°C when the DOC is combined to plasma reactor. This value has to be compared to 197°C obtained in the case of DOC thermal catalysis (T₅₀ improvement of about 57°C).

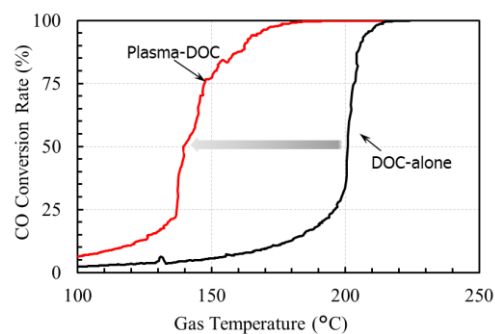


Fig.4: CO light-off curves for DOC and plasma-DOC configuration (GHSV=55 000 h⁻¹, SIE=85 J/L).

HCs conversion efficiency was measured under the same experimental conditions as those of CO and data are shown in the Fig. 5. For catalyst-alone configuration, a decrease of the HCs conversion (*i.e.* rise of the concentration of HCs) is observed over the course of the experiment. This is due to the dynamics of HCs storage of the DOC which in turn become more and more saturated with HCs (HCs adsorbers) during the experiment. HCs are partially stored before begins to be released at a temperature of about 100°C. Desorption process starts at 140°C while the DOC was not activated yet. The decrease of HCs concentration at about 197°C shows the beginning of DOC activation and T₅₀ is reached at 201°C. When the plasma was coupled with downstream DOC, hydrocarbons conversion rate is always higher than 50%. In that case, T₅₀ of HCs corresponds to the temperature at which the HCs conversion rate starts to increase (168°C). From these data, T₅₀ is improved by about 33°C and the HCs peak release in the atmosphere is avoided. Increasing the space velocity (GSHV) from 55 000 to 82 000 h⁻¹ leads to the same behaviour with lower T₅₀ light-off temperature improvement. Overall, the performance improvement made by combining plasma and Diesel oxidation catalyst in the post-discharge appears clearly in these studies.

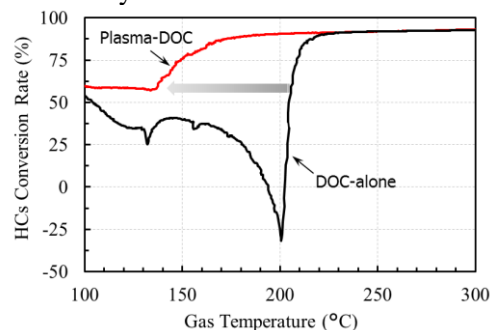


Fig. 5: HCs light-off curves for DOC and plasma-DOC configuration (GHSV=55 000 h⁻¹, SIE=85 J/L).

As expected, the plasma reactor totally oxidizes NO to NO₂ at low temperature. This oxidation

was greatly promoted by the hydrocarbons present in the exhaust. The interactions between NO_x (NO+NO₂) and HCs are interesting not only for NO_x chemistry, but also at low temperatures for the oxidation of hydrocarbons, a subject extensively investigated in combustion domain (cold flame and ignition phenomena). When combined to catalyst the situation was completely different. Fig. 6 presents NO and NO₂ concentrations as a function of gas temperature for DOC-alone and plasma-DOC at specific input plasma power. By comparing the data, several observations may be made. First, before the catalyst activation (~200°C), NO₂ produced by the plasma was stored into the DOC (a part could be reduced to NO by reactions with CO and HCs). As the exhaust temperature approach 200°C, the catalyst becomes active and NO to NO₂ oxidation began. Increasing the plasma input power leads to decrease the activation temperature (150°C at 280 W compared to 175°C at 200 W).

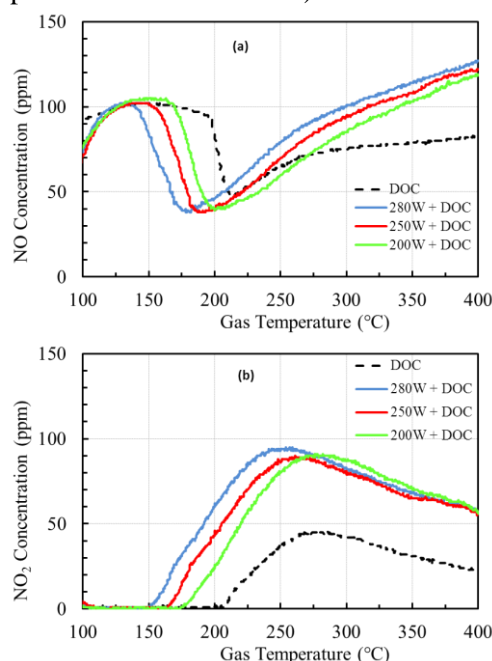


Fig 6: NO and NO₂ Concentrations for DOC and plasma-DOC vs gas temperature for different plasma energy deposition.

4. CONCLUSION

The use of non-thermal plasma to assist Diesel oxidation catalyst (Pt-Pd/Al₂O₃) was studied in synthetic gas simulating HCCI Diesel exhaust. Particular attention has been paid to HCs, CO, and NO_x oxidation efficiencies for both DOC and plasma-DOC systems. Light-off temperature T₅₀ of DOC for CO in test bench scale can be improved by 57°C when catalyst is combined

downstream the non-thermal plasma reactor. The use of non-thermal plasma reactor could be a new approach to improve the emission control, especially during the engine cold start phase.

To well understand the interaction between the plasma and the catalyst, it would be important to measure the temperature at the catalyst surface (inside the catalyst itself). This will provide information on the exothermic reactions involving plasma reactive species and catalyst active sites. Studies are in progress and results will be presented.

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