

# Plasma-Assisted Diesel Oxidation Catalyst on Bench Scale: Focus on Light-off Temperature and NO<sub>x</sub> Behavior

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Published online: 23 February 2013  
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**Abstract** The effect of a non-thermal plasma reactor over a commercial Diesel oxidation catalyst (DOC) was investigated. Studies have been focused on the gas treatment efficiency together with lowering light-off temperature when a DOC catalyst was connected downstream to plasma reactor in test bench scale. Experiments have been conducted using multi-DBDs (dielectric barrier discharge) reactor in planar configuration driven by a HV AC generator (11 kV–15 kHz). The specific input energy was set to 57 and 85 J/L. Experiments were performed in gas composition simulating Diesel exhaust. Commercial DOC, monolith-supported Pt–Pd/Al<sub>2</sub>O<sub>3</sub>, was used at gas hourly space velocities of about 55,000 and 82,000 h<sup>-1</sup>. CO and hydrocarbons light-off curves were determined for DOC, plasma, and plasma-DOC systems by temperature programmed surface reaction from 80 to 400 °C. Particular attention has been paid to the gas temperature between the plasma reactor and the DOC. Results show that the plasma-catalyst system provides the lowest light-off temperatures for CO and HCs. Under conditions of this study, light-off

temperature improvement by about 57 °C was obtained and the plasma reactor totally oxidized NO to NO<sub>2</sub> at low temperature.

**Keywords** Diesel oxidation catalyst · Non-thermal plasma · Light-off temperature · NO<sub>x</sub>

## 1 Introduction

A key feature of Diesel oxidation catalyst (DOC) is its ability to oxidize efficiently CO (carbon monoxide) and unburned hydrocarbons (HCs) at the Diesel exhaust temperature levels. While the DOC technology has progressed to the point where CO and HCs emissions can be greatly reduced, there remain issues of cost and low temperature activity. It is important to start the CO and HCs conversions as soon as possible after engine start (i.e. cold start regime) to reduce harmful emission. In Diesel applications, these requirements are generally achieved by the use of high noble metal loadings and HCs adsorbers [1–4].

Among several approaches under development in the last decade, the research efforts are focusing on finding a catalyst that can be combined with non-thermal plasma (NTP) to reduce pollutants from lean exhausts and especially for Diesel exhaust [5–7]. In that field, corona discharges and DBD (dielectric barrier discharge) in conjunction with number of materials having catalyst activity for NO<sub>x</sub> reduction in lean exhaust have been studied extensively [8, 9]. To be effective, this technology should improve pollutant conversion efficiencies and lower catalyst light-off temperature.

This paper will present the results of extensive series of experiments in test bench scale aimed towards understanding the effect of the non-thermal plasma on the

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activation of a Diesel oxidation catalyst and on the NOx conversion chemistry. The effectiveness of the processes with regard to NO, NO<sub>2</sub>, CO, HCs removal and light-off temperature of the DOC catalyst for CO and HCs lowering was discussed.

## 2 Experimental

The experiments were conducted in the Renault test bench facility. The experimental arrangement, shown schematically in Fig. 1, consists of a continuous flow gas generation and heating systems, a DBD reactor, and a gas detection system.

The gas feed stream simulating Diesel exhaust during the experiments contained mixture of O<sub>2</sub> (10 %), CO<sub>2</sub> (4 %), CO (8,500 ppm), HCs (1,500 ppmC), NO (100 ppm), H<sub>2</sub>O (4 %), and N<sub>2</sub> (balance) was prepared in a gas handling system and concentration of each gas was controlled by calibrated high-precision mass flow controllers. Two series of experiments have been conducted at two different total flow rates: 176 and 262 L/min which are equivalent to GHSV (gas hourly space velocity) of about 55,000 and 82,000 h<sup>-1</sup>, respectively.

The plasma reactor we used is multi-DBDs reactor in planar geometry provided by HK-MnS Company according to our technical specifications. 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. 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 canning. Figure 2 show photography of the plasma reactor operating under nitrogen flow.

To characterize the electrical energy consumption of the process, the mean electric power dissipated in the plasma was calculated from the applied voltage *u*(*t*) and discharge current *i*(*t*) by the following formula:

$$P(W) = \int_0^T i(t) \cdot u(t) dt$$

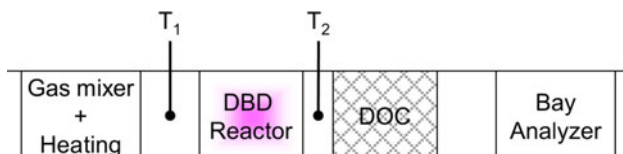


Fig. 1 Schematic diagram of the experimental set-up

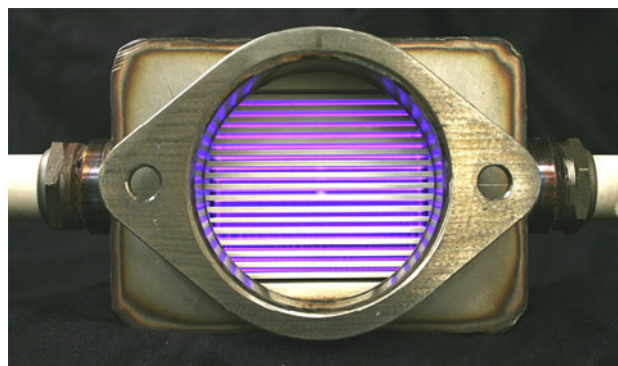


Fig. 2 Photography of the plasma reactor and discharges in N<sub>2</sub>

The applied voltage and the current were measured using a high voltage probe (Tektronix P6015A) and current probe (Pearson 4001), respectively. The output signals were transmitted to a digitizing oscilloscope (Tektronix DPO 3054).

The specific input energy (SIE) which is the energy deposition of the investigated discharge can be defined as the energy deposited per unit volume of gas in the plasma reactor at standard conditions (25 °C and 1 atm). It can be expressed by the following equation:

$$SIE(J/L) = \frac{P \text{ (discharge power (W))}}{Q \text{ (gas flow rate (L/s))}}$$

In this work, experiments were conducted at energy deposition of about 57 and 85 J/L.

A commercial Euro 5 Diesel oxidation catalyst (honeycomb structure monolith-supported Pt–Pd/Al<sub>2</sub>O<sub>3</sub> ratio 2/1) was used in these experiments. The sample catalyst was hydrothermally aged for 5 h at 750 °C under N<sub>2</sub>–O<sub>2</sub>–10 % H<sub>2</sub>O mixture.

CO and HCs light-off curves were determined for DOC only, plasma only, and plasma-DOC systems by TPSR (temperature programmed surface reaction) for temperature in the range 80–400 °C and space velocity of about 55,000 and 82,000 h<sup>-1</sup>. Temperatures at different positions on the axis of the system (x-axis) were measured using K-type thermocouple probes. The temperature T<sub>1</sub> is that of the upstream of the plasma reactor thermocouple, T<sub>2</sub> is that of the upstream of the catalyst thermocouple (see Fig. 1).

For all experiments, the exiting gas compositions were measured using Pierburg bay analyzer (AMA 2000) for O<sub>2</sub>, CO<sub>2</sub>, CO, HCs, NO and NO<sub>2</sub>. Preliminary tests verified accuracy of the concentrations of the NO and NO<sub>2</sub> to ±2 ppm, and CO, CO<sub>2</sub>, and HCs to ±5 %. Ozone was also measured at downstream of the plasma reactor with an ozone analyzer (IN USA—IN-2000).

### 3 Results and Discussion

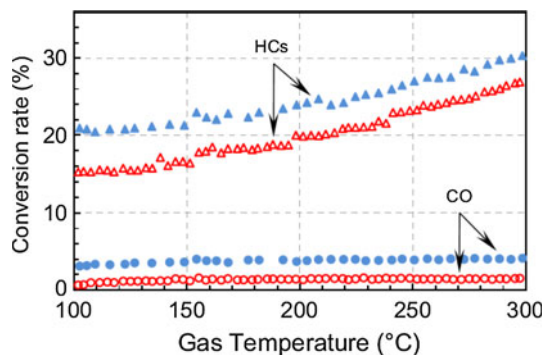
Different set of experiments were conducted to evaluate the effect of the plasma discharges on an exhaust in the presence or not of Diesel oxidation catalyst. We first present results without catalyst to show that the plasma gas exhaust produces the active intermediate species needed for the activation of the catalyst. Then, results for DOC and plasma–DOC combination obtained in the same experimental conditions are presented.

#### 3.1 Plasma Only

A difference between conventional catalytic and plasma activated reactions is that in the latter many active species, free energized electrons, ions, and UV light are generated at room temperature. Under oxygen-rich conditions, a fraction of input plasma energy is dissipated in the dissociation of  $O_2$  which become the dominant process in the production of radicals which is the initiator of the hydrocarbon chemistry according a well-established reaction pathway [9–12]. Analysis of gas composition at outlet of the plasma reactor in the laboratory-scale experiments revealed the existence of compounds already reported in the literature [13, 14]. We should highlight the presence of aldehyde ( $CH_2O$ ), R-NOx ( $CH_3ONO_2$ ), formic acid ( $CH_2O_2$ ) and nitrogen dioxide ( $NO_2$ ).

Temperature programmed CO and HC oxidation experiments were performed and data for energy deposition of 57 and 85 J/L are shown in Fig. 3. The hydrocarbons oxidation conversion by plasma discharges increases as the inlet gas temperature increases. The maximum oxidation rate of about 30 % was obtained at 85 J/L. HCs totally or partially ( $C_xH_yO_z$ ) oxidized can prevent the poisoning of the actives sites and could contribute to decrease the DOC activation temperature.

Several strategies (close-coupling, fuel-burning catalyst heaters, electrically heat catalysts) exist to quickly warm-

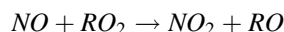
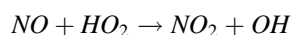


**Fig. 3** HCs and CO oxidation by plasma as a function of upstream gas temperature ( $T_1$ ): SIE = 57 J/L (open symbols) and SIE = 85 J/L (close symbols)

up the catalyst to its operating temperature in order to improve the catalyst light-off for HCs and CO oxidation [2–4]. However, the active intermediate species or “by-products” created by the plasma discharges could generate, at the surface of the DOC, exothermic reactions that could permit the fast heating of the catalyst.

Concerning CO oxidation, the plasma discharges seems to have a marginal effect in the input energy explored in that study. A maximum conversion rate of about 3 % at 85 J/L was measured whatever the gas temperature in the range 80–300 °C.

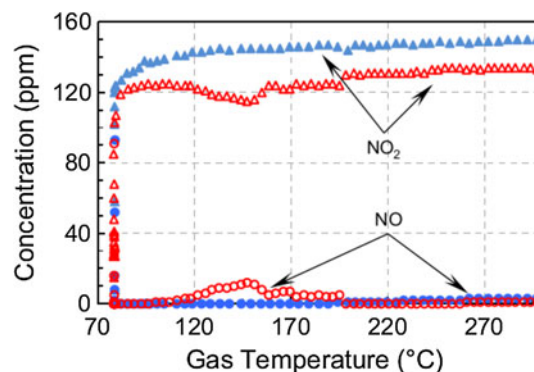
Figure 4 presents NO and  $NO_2$  concentrations at the outlet of the plasma reactor as function of the inlet gas temperature. As expected, the plasma reactor totally oxidizes NO to  $NO_2$ . This conversion was greatly promoted by the hydrocarbons present in the exhaust. The NO/ $NO_2$  oxidation could be described by the following reaction where R represents the hydrocarbon radical [6, 9, 13, 14]:



One can note that in these experimental conditions, NOx ( $NO + NO_2$ ) concentration measured at the outlet of the plasma reactor is higher than the NO inlet concentration (100 ppm) especially at high energy deposition. Decreasing the SIE could decrease the NOx production. As example, at 57 J/L and 300 °C, the NOx concentration decreased from 150 to 135 ppm.

Ozone was not detected in these experiments even at low temperature as reported in the literature [5]. This means that the ozone is effectively produced by the plasma reactor (proved in our laboratory-scale experiments) but quickly reacts to oxidize species such as NO and HCs.

The interactions between NO and HCs are interesting not only for NOx chemistry, but also at low temperatures for the oxidation of hydrocarbons, a subject extensively



**Fig. 4** NO oxidation by plasma as a function of upstream gas temperature ( $T_1$ ): SIE = 57 J/L (open symbols) and SIE = 85 J/L (close symbols)

investigated in combustion domain (engine knock, cold flame and ignition phenomena).

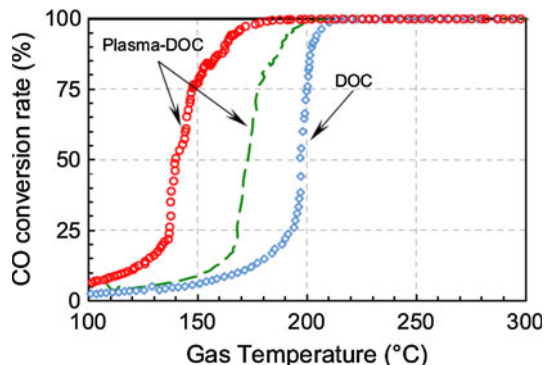
### 3.2 DOC and Plasma-DOC Combination

The first step was to characterize the light-off temperature of the DOC for CO and hydrocarbons oxidation. Light-off temperature is generally defined as the temperature at which the conversion rate of gaseous constituents reaches the 50 % level ( $T_{50}$ ). We focus on temperature  $T_{50}$  values for CO and HCs in the case of DOC and plasma-DOC combination. Figure 5 shows the light-off curves for CO measured with the catalyst downstream of the plasma reactor at GSVH of about 55,000  $\text{h}^{-1}$  and energy deposition of about 85 J/L for the two configurations.

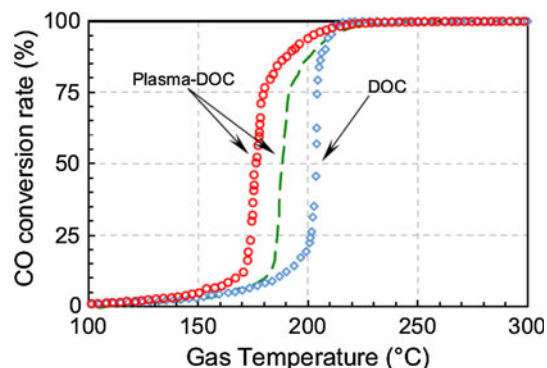
Considering the gas temperature measured by the thermocouple  $T_1$  (upstream of the plasma reactor),  $T_{50}$  temperature for CO is about 140 °C when the DOC is combined to plasma reactor. This value has to be compared to 197 °C obtained in the case where only the DOC is used (without plasma reactor). If we take into account the additional heating due to the plasma reactor (gas temperature measured by the thermocouple  $T_2$  in the plasma-DOC configuration), the improvement of  $T_{50}$  temperature for CO is about 24 °C instead of 57 °C obtained in the first case. In addition to heat the gas, the plasma reactor improves the DOC efficiency toward the low temperatures.

The gas flow has an important impact on the plasma and the catalyst chemistry. While increasing the gas flow, the specific input energy (SIE) decreases together with decreasing the residence time leading to shorter contact time between the chemical species and the catalyst. As illustrated in Fig. 6, when the space velocity varies from 55,000 to 82,000  $\text{h}^{-1}$ , the  $T_{50}$  temperature for CO increase from 197 to 204 °C in the case of DOC configuration.

In presence of a plasma reactor, the  $T_{50}$  temperature for CO is reduced by 28 °C (16 °C if we take into account the



**Fig. 5** CO light-off curves for DOC and plasma-DOC configuration for GHSV = 55,000  $\text{h}^{-1}$  and SIE = 85 J/L. Open symbols referred to temperature  $T_1$  and dash line referred to temperature  $T_2$



**Fig. 6** CO light-off curves for DOC and plasma-DOC configuration for GHSV = 82,000  $\text{h}^{-1}$  and SIE = 57 J/L. Open symbols referred to temperature  $T_1$  and dash line referred to temperature  $T_2$

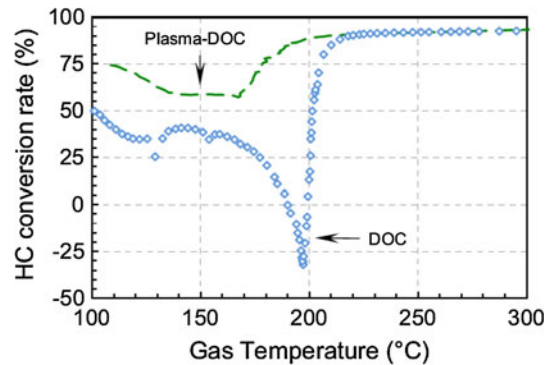
additional heating due to the plasma reactor). We notice that the additional heating induced by the plasma reactor is limited (<35 °C in all cases).

HCs conversion efficiency was measured under the same experimental conditions as those of CO and data are shown in the Fig. 7. HCs light-off curve indicates the presence of HC adsorbers in the DOC.

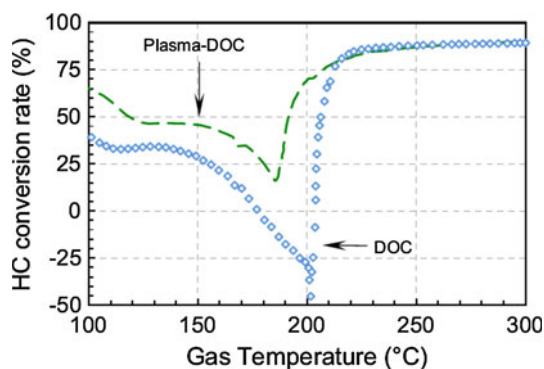
For DOC configuration, the hydrocarbons partially stored before begins to be released at a temperature of 100 °C. Desorption process starts at 140 °C while the catalyst was not activated yet. The decrease of hydrocarbon concentration at about 197 °C shows the beginning of DOC activation and  $T_{50}$  is reached at 201 °C.

In plasma-DOC combination, HC conversion rate is always higher than 50 %. In that case,  $T_{50}$  of HCs corresponds to the temperature at which the HC conversion rate starts to increase and corresponds to about 168 °C.  $T_{50}$  of HCs is improved by 33 °C and the HCs peak release in the atmosphere is avoided.

We observed the same behavior concerning the HCs light-off curve as illustrated in Fig. 8 when the space



**Fig. 7** HC light-off curves for DOC and plasma-DOC configuration for GHSV = 55,000  $\text{h}^{-1}$  and SIE = 85 J/L. Open symbols referred to temperature  $T_1$  and dash line referred to temperature  $T_2$



**Fig. 8** HC light-off curves for DOC and plasma-DOC configuration for GHSV = 82,000 h<sup>-1</sup> and SIE = 57 J/L. *Open symbols* referred to temperature T<sub>1</sub> and *dash line* referred to temperature T<sub>2</sub>

velocity varies from 55,000 to 82,000 h<sup>-1</sup>. The T<sub>50</sub> temperature for HCs decreased from 207 to 192 °C when comparing DOC and plasma-DOC curves, respectively. The increasing of GSVH from 55,000 to 82,000 h<sup>-1</sup> leads to increase the CO and HCs T<sub>50</sub> value for both two configurations. Despite this fact and in all cases studied, the non-thermal plasma shows a benefit effect in improvement of the CO and HCs T<sub>50</sub> temperature of the catalyst.

#### 4 Conclusion

The use of non-thermal plasma to assist Diesel oxidation catalyst (Pt–Pd/Al<sub>2</sub>O<sub>3</sub>) was studied in synthetic gas bench simulating Diesel exhaust. Particular attention has been paid to HC and CO oxidation efficiencies for both DOC and plasma-DOC systems. Light-off temperature T<sub>50</sub> 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 main advantage of the non-equilibrium plasma is to combine both the low gas heating (few tens of °C) and the chemical effects (reactive species, by-products...) at low temperature to improve the DOC activity. The use of non-thermal plasma reactor could be a new approach to

improve the emission control, especially during the engine cold start phase. Also, the plasma reactor can play a role in the improvement of NH<sub>3</sub>-SCR at cold start by controlling the NO/NO<sub>2</sub> ratio at low temperature.

More work is needed in order to well understand the interaction of the plasma active species and the catalyst. These species could be involved in exothermic reactions which contribute to heat the surface of the catalyst. It would be important to measure the catalyst surface temperature by means of thermocouple probes placed inside the catalyst itself. Studies have been done and results will be presented in a forthcoming paper.

**Acknowledgments** The authors gratefully acknowledge Kim Yone-Seung, Baek Sung-Joon, and the plasma group of HK-MnS Company Ltd (Korea) for their fruitful discussions and technical support. This study was supported by national French CIFRE program (agreement no. 774/2009) with a financial support of Renault SA Company.

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