

Post-treatment for the next Generation Of Diesel Engines

PAGODE

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3	Johnson Matthey	JM
4	Institut Français du Pétrole	IFP
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1. Project Objectives and Organization

1.1. Project Objectives

The aim of the PAGODE project is to provide a comprehensive, system oriented development approach on potentially new after treatment processes that will be required by the next Homogeneous Charge Compression Ignition (HCCI) combustion systems, taking into account the future fuel generations. This project works through 4 main identified and focused directions:

1. **Work Package 1:** Low Temperature Oxidation of CO and HC: fuel effect and oxidation mechanisms in advanced homogenous combustion processes
2. **Work Package 2:** Advanced new catalyst formulations for high CO, HC concentration and low temperature oxidation
3. **Work Package 3:** Emerging flexible low temperature oxidation technologies
4. **Work Package 4:** System synthesis for next powertrain generation

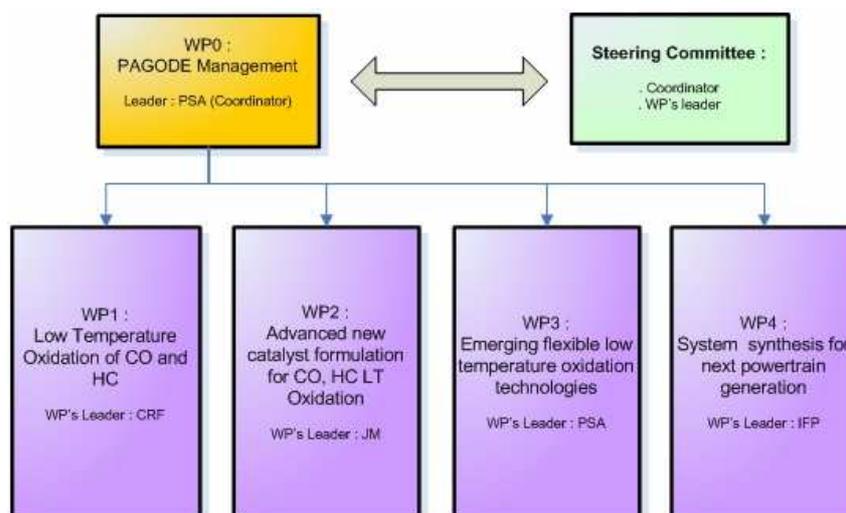
The scientific objectives of this project are:

- **Understand the complex kinetic mechanisms** and chemical principles of CO/HC low temperature oxidation for the next generation Diesel engines exhaust environment,
- **Develop a robust, efficient, and accurate computational models** to analyze, simulate and improve the performance of next generation catalytic converters (a transient one-dimensional model, and a single spatial dimension will be developed at a first step and then 2D and 3D calculations will be investigated and integrated).

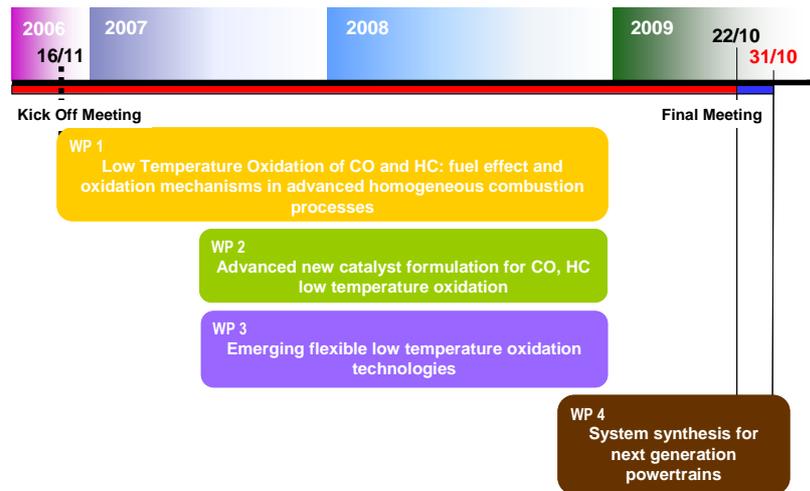
The technological objectives are:

- **Formulate, develop, test and optimize advanced new catalyst formulation** for CO/HC low temperature oxidation,
- **Design, develop and test emerging flexible low temperature oxidation technologies based on plasma concepts,**
- Perform a **powertrain system synthesis** and evaluate, for next generation power trains, the needed requirements and boundary conditions to implement at their best the advanced after treatment processes in diesel engines.

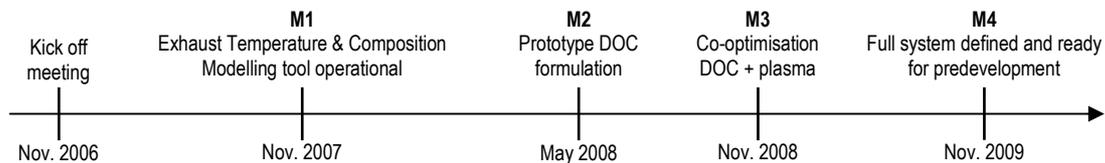
1.2. Project Organization



1.3. Project Roadmap



1.4. Project Milestones Plan



2. Main Achievements

2.1. WP1: Low Temperature Oxidation of CO and HC

2.1.1. Introduction

The transverse work package WP1 (Low temperature oxidation of CO/HC) was dedicated to the scientific and research activities on low temperature oxidation of high levels of CO and HC emissions, as created by HCCI-like combustion modes. This item was divided into data collection, complementary emissions measurements and modelling parts. From data collection and complementary emissions measurements part, the main objective was to get reliable data on CO and HC emissions and exhaust temperatures for the further system definition and to supply boundary conditions for the simulations tools. The modelling aim was then the development of innovative tools for the design and the improvement of exhaust lines using the developed advanced catalytic devices.

In details, WP1 was divided in three tasks:

- Task 1.1: Characterization of emissions levels typical of homogeneous combustion modes
- Task 1.2: Modelling tool development
- Task 1.3: Assessment the developed software tool and integration

2.1.2. Task 1.1: Characterization of emissions levels typical of homogeneous combustion modes

The assembling, set-up, deep characterization of HCCI engine was in charge of IFP.

The first phase was devoted by IFP to the Renault engine modification for the HCCI combustion capability. This adaptation includes a reduction of the compression ratio from 17.7:1 to 14:1 with a dedicated piston chamber based on NADI™ concept, a narrow injector cone angle realized in accordance with pistons chamber and a reduction of the swirl number. A high permeability and high cooling efficiently prototype EGR circuit was also manufactured and installed on the prototype engine.

The second phase was dedicated to HCCI operating points calibration, with the state-of-the-art strategies developed at IFP. Operating points were selected in order to be representative of real driving conditions:

- 850 rpm – no load (idle, warm conditions)
- 1500 rpm – 2 bar of BMEP (warm and cold conditions, standard and B10 fuel)
- 1500 rpm – 4 bar of BMEP (warm conditions)
- 2000 rpm – 5 bar of BMEP (warm conditions)

The obtained results are in accordance with the state-of-the-art results of the NADI™ concept. According to temperature analysis (inlet and outlet turbine), HCCI does not significantly modify the exhaust gas temperature level compared to Euro 4 combustion. This result was expected from bibliographic study and confirmed by CRF internal data. It may be considered as a very positive result regarding the after-treatment issue.

In HCCI mode, CO and HC emissions showed wide raise compared to conventional mode. The experimental data as well as data collected from CRF internal activities showed an increase factor of 2-3 in the case of CO and up to a factor 4-5 in the case of hydrocarbons. On the other hand, NO_x emission in HCCI mode was about the half compared to conventional mode and the PM emission reduction was estimated even up to one order of magnitude (Figure 1).

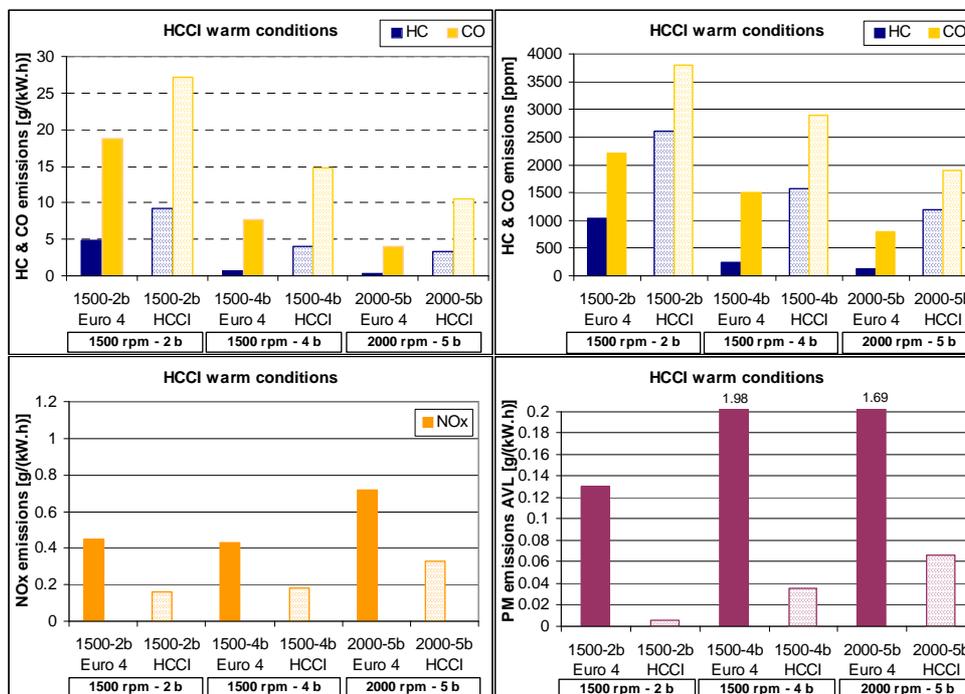


Figure 1. Results for HCCI warm conditions

Concerning the fuel consumption, results obtained under HCCI combustion were very close to those obtained in conventional combustion. Detailed analysis of exhaust emissions were carried out. The engine-out results showed that the HC repartition was quite similar in HCCI and in Euro 4 combustion,

including HC in the C1-C9 range, aldehydes and ketones. However, as the absolute level of HC was higher at HCCI engine-out, the absolute level of each species was also higher. Figure 2 reports the main HC detected species.

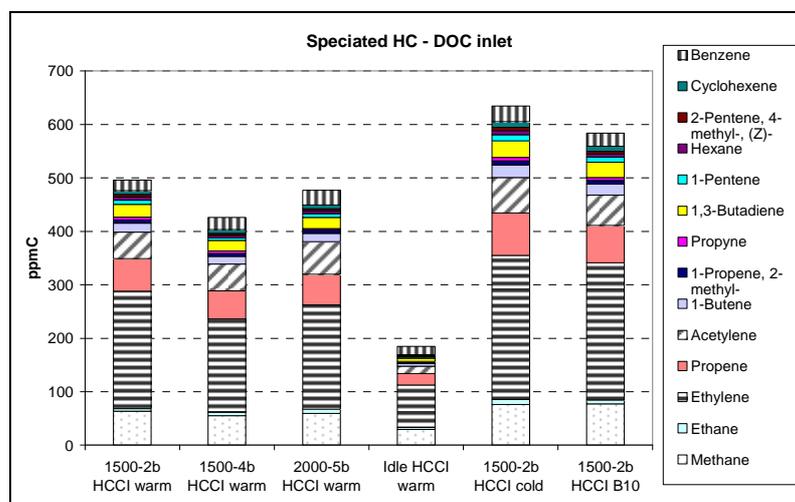


Figure 2. HC speciation - DOC inlet

A Euro 4 oxidation catalyst was tested in order to evaluate strong and weak points of the current technology and selected as a reference for the following PAGODE tasks. Tests showed that pollutant emissions were efficiently converted by the catalyst when active, including harmful emissions of benzene, 1,3-butadiene and formaldehyde. At idle, the temperature was too low and no pollutant species could be treated. The tests also showed that there was mainly methane remaining after DOC. This pollutant is particularly hard to treat with classical formulation. From PAGODE tests, only 10% was successfully converted at 470°C. Therefore it should be necessary to improve both the light-off performance of the catalyst and the methane oxidation efficiency to comply with the future standards. Finally, with B10 fuel, NO_x, HC and CO emissions were slightly lower than with standard fuel, while PM emission was slightly higher.

This preliminary study provided boundary data for the development of innovative software tools (inside WP1), for the design of suitable catalyst regarding HCCI emissions (WP2) and for the development of the advanced technique of non-thermal plasma (WP3).

2.1.3. Task 1.2: Modelling tool development

2.1.3.1. Kinetics experiments

APTL experimentally investigated Diesel oxidation catalyst (DOC) kinetics under conditions of lower temperatures and more pronounced inhibition phenomena than is normally encountered by existing DOC applications. Dedicated laboratory experiments and model-based data reduction were the main tools employed to obtain updated kinetic parameters and inhibition factors for the catalysts considered.

The conversion results obtained from Temperature Programmed Oxidation (TPO) experiments with a single pollutant were used for tuning the Arrhenius-type rate constants and activation energies for the DOC model reaction rate expressions. TPO experiments with two reactants considered one of the reactants as the primary (fixed feed concentration) and varied the concentration of the inhibitory reactant in order to determine constants in the inhibition (inverse kinetic) expressions. An iterative approach was necessary in order to obtain a set of DOC model parameters that simultaneously satisfy

all the conversion results from relevant experiments. For this data reduction, a form of the DOC model suitable for the case of the powder bed reactor was employed. The adapted DOC model was run with the boundary/inflow conditions of each of the experiments repeatedly until the model response described the experimental measurements. In this procedure, the actual catalyst bed temperature distribution was obtained by model calculations using the temperatures of a thermocouple upstream of the reactor and the oven thermocouple (outside wall of reactor). An example of the matched DOC model conversion and the resulting shift from measured/upstream to actual catalyst bed (average) temperature can be seen in Figure 3 for the case of the TPO of C_3H_8 at 1000 ppm feed concentration. The same procedure was applied to all other kinetics experiments in an iterative manner, enabling a complete set of widely applicable DOC model parameters to be obtained for the subsequent DOC modelling development.

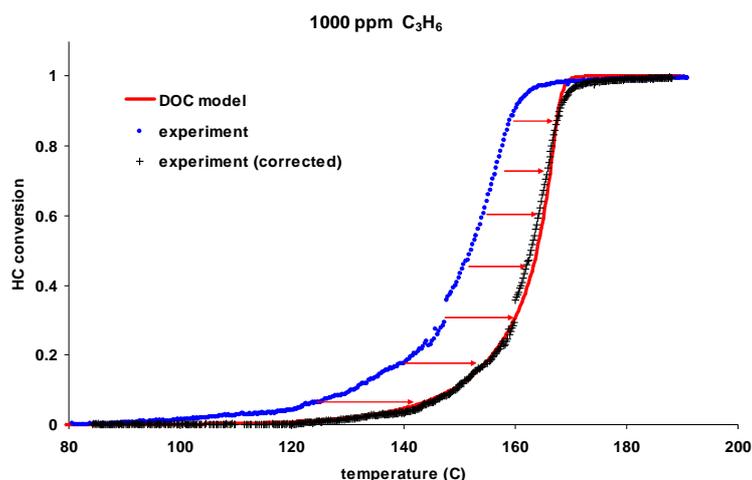


Figure 3. Example result from the kinetics determination analysis using the powder bed reactor version of the DOC model

2.1.3.2. DOC simulation tool

In parallel to the experimental campaign, APTL developed a novel simulation tool for investigation of DOC exhaust after-treatment performance including the effects of non-uniformity in the boundary conditions (e.g. inflow temperature profile) or DOC characteristics (e.g. zoned coatings). This involved the development of a model for a single DOC channel and its embedding within a widely available CFD solver so as to be applicable to 2-D and 3-D simulations.

The core DOC model implementation (module) was based on a formulation including the necessary elements for the lower exhaust temperatures and high CO, HC concentrations investigated in the PAGODE project. In particular, the DOC model formulation included treatment of reaction and inhibition of two hydrocarbon families (“fast” and “slow” oxidising hydrocarbons represented by C_3H_6 and C_3H_8) as well as their storage behaviour in zeolitic material. The rate expressions for reaction and adsorption processes were coupled to expressions for the conservation of mass and energy along the length of a converter channel in the so-called single channel formulation which considers also the heat transfer in the solid phase.

The single-channel model, programmed as a set of subroutines/functions in FORTRAN, was then integrated as an external library/module for 2-D/3-D calculations within the CFD solver FLUENT 6.3.26, forming a simulation tool capable of considering spatial non-uniformities in DOC operating conditions. The numerical coupling of the core DOC module with a CFD model of an actual converter geometry was

achieved through the development of a set of interfacing functions (in the C language) conforming to the User-Defined Function (UDF) facility of the FLUENT 6.3.26 CFD software. Example results (2-D calculations) of initial use of the modelling tool developed are shown in Figure 4.

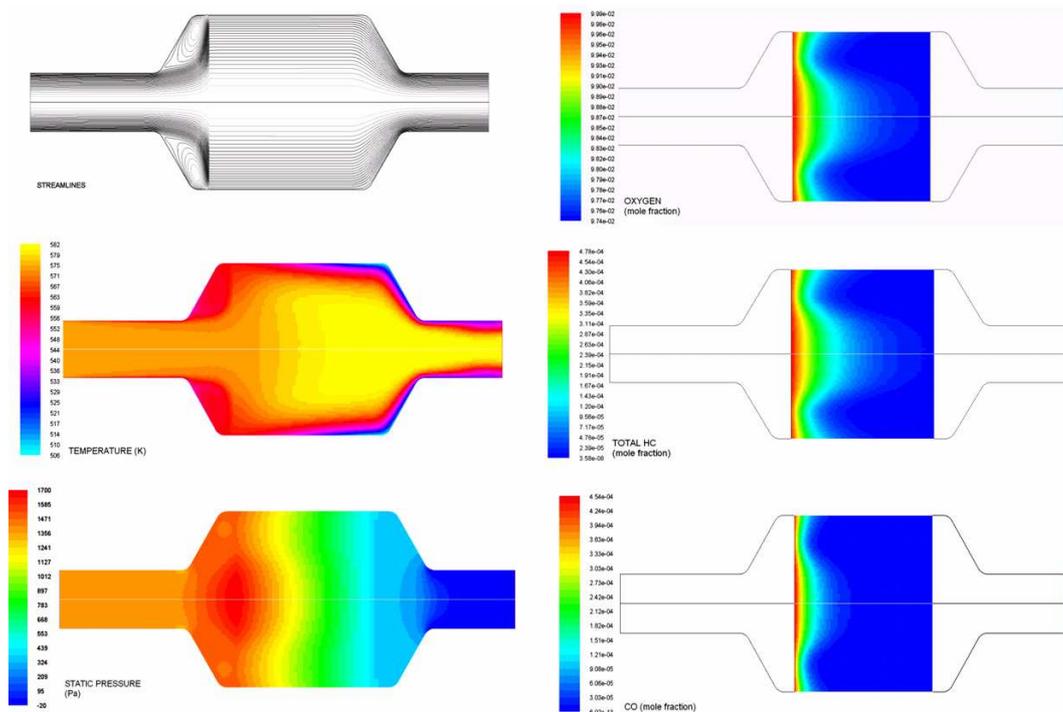


Figure 4. DOC simulation tool results for a 4.0" x 5.66" DOC with the REF catalyst formulation, 400 cpsi / 6 mil monolith, with a feed of 500 ppm CO, 500 ppm hydrocarbons concentration, at an exhaust inflow temperature of 350°C. External canister temperature was 250°C

2.1.3.3. Storage parameters from CRF data

CRF supported APTL in order to provide data specifically targeted for the storage behaviour of PAGODE catalysts. Propylene was identified as the main species to be associated to storage (and desorption) phase among the selected hydrocarbons. An oxygen storage effect could be moreover clearly identified. Such experimental results were used to determine values for the relevant Arrhenius expression of the adsorption-desorption parameters by iteratively finding the DOC simulation tool response that describes the experimental time series of hydrocarbon species concentrations. Strongly differing storage dynamics were seen in the measurements and this was reflected in the resulting calculated storage model parameters.

2.1.4. Task 1.3: Assessment the developed software tool and integration

The assessment the developed software tool and integration phase were carried out according the following steps:

- Implement the APTL model and User Defined Functions (UDF) in Ansys FLUENT
- Integrate boundary conditions characteristic of CRF test conditions
- Simulate the experimental tests carried out in WP2
- Evaluate the accordance between the virtual and experimental results
- Modify and improve the model in order to be closer to experimental results by an iterative software tool integration phase between APTL and CRF

- Finally, evaluate transient/cycle response accuracy against transient test bench measurements

It was decided to simulate the tests carried out in WP2. Such experiments (Synthetic Gas Bench tests) had the objective of select the best formulation during the catalyst development phase carried out by Chalmers University and Johnson Matthey. CRF tests were carried out on lab-scale samples, representative of the real conditions in terms of temperatures, gases and space velocity.

Two different testing protocols were adopted. The first one was characterised by a hydrocarbon mixture of butane, pentane, hexane while the second one was characterised by ethylene, methane and propylene mixture (ratio 3.5:1:1) in accordance with the IFP speciation on the first part of WP1. Both the experimental protocols were simulated.

First protocol simulation results highlighted important differences between simulated and experimental results. Figures 5 and 6 report the comparison results relating to the second protocol concerning both the static (standard) and dynamic (CO pulsing) light-off tests: good accordance can be seen if the comparison is made with the aged results. Such good accordance can be highlighted not only in terms of T50 light-off, but also in the conversion efficiency trend all along the investigated temperature.

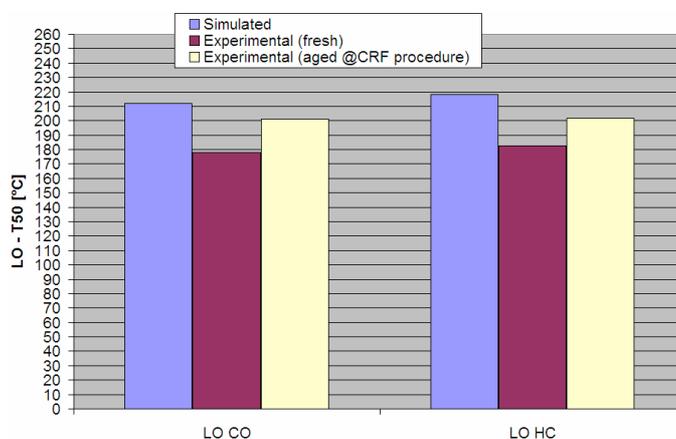


Figure 5. Static light-off results on second protocol

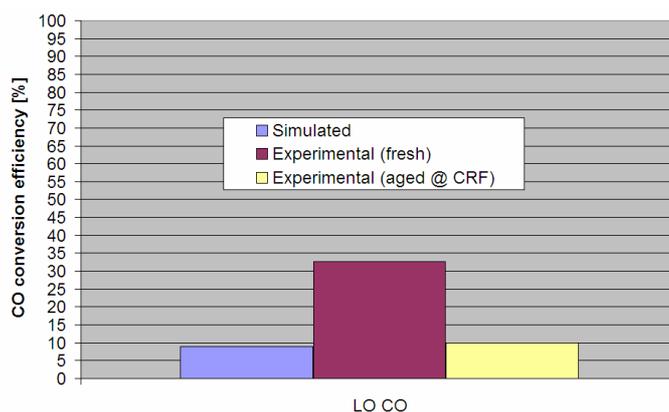


Figure 6. Dynamic light-off results on second protocol

The DOC simulation tool transient response was also evaluated against transient engine bench tests (aged catalysts) performed by IFP on the REF, DEVG and DEVJ formulations. The DOC model was found capable of meeting the $\pm 10\%$ cumulative cycle simulation accuracy target for a number of the catalyst formulations and emissions measurements. The necessity for further addition of CO storage/buffering was found from this evaluation, in particular for catalysts such as DEVJ which show dominant CO storage phenomena in the low ($< 200^\circ\text{C}$) exhaust temperature response.

2.2. WP2: Advanced new catalyst formulation for CO, HC and LT oxidation

2.2.1. Introduction

During WP2, fundamental investigation of advanced catalyst formulation for low temperature oxidation of high level of CO and HC was performed by Chalmers University in collaboration with CRF and JM. The work carried out between the three partners allowed us to determine the best catalyst components and preparation route to use for improved catalytic activities in respect to HCCI conditions. Newly developed technologies were benchmarked against the Johnson Matthey reference catalyst, current commercially available technology (JM ref). Scale up studies of the new formulation (JM) and synthetic gas bench measurements (JM and CRF) were carried out to ensure that the newly developed catalyst has the same properties as the catalyst powder developed previously by Chalmers University. Progresses in terms of catalyst performance, conversion efficiency, low light-off temperature, poisoning effects, durability and precious content metal were monitored and reported during the project. Test conditions and aging procedures optimisations were carefully investigated. Determination of kinetic data for the best catalyst were performed and implemented in WP1. Chalmers University also identified the potential impact on the new formulation of specified secondary emissions from the plasma reactor from WP3. The best technologies were finally prepared on full size monolith and submitted for engine test in IFP for WP4.

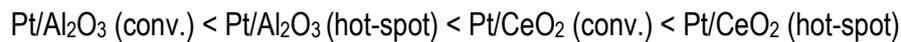
2.2.2. Task 2.1: Fundamental investigation of new catalyst formulation on the basis of specified exhaust chemical specification and temperatures measurements from WP1

The first task within this work was to investigate new potential catalyst formulations based on specified chemical speciation and temperature measurements from WP1. This fundamental investigation, of potential new catalyst formulations for low temperature oxidation of high levels of CO and HC, was carried out by Chalmers University with the support of CRF and Johnson Matthey. Chalmers synthesised and characterised two generation of model catalysts and also performed activity studies. JM and CRF provided support to Chalmers during the catalyst formulation development. Catalysts concepts utilising i) exothermic reaction heat (Pt hot spot formulation) and ii) the support material (Al_2O_3 vs. CeO_2) were identified. Identification of any issues regarding catalyst components, which may cause problems during scale up, was discussed.

Monolithic Pt/ $\gamma\text{-Al}_2\text{O}_3$ and Pt/ CeO_2 catalysts were prepared by depositing of the platinum phase, either homogeneously or heterogeneously (*i.e.*, local high platinum concentration), in the washcoat. Platinum (Pt) was chosen as a reference. Focus was placed on distribution of the active phase. Alumina ($\gamma\text{-Al}_2\text{O}_3$) was chosen as a reference support because of its high surface area, it is commercially available and preparation routes are very well known. Ceria (CeO_2) was chosen as an alternative support to improve cold start, because of its high oxygen storage capacity, its high oxygen mobility and water gas shift reaction involved.

Chalmers University demonstrates that Pt distribution as well as support material affects the low-temperature activity for CO and HC oxidation. Activity tests of prepared catalysts using synthetic HCCI exhausts, *i.e.* oxidation of CO, CH_4 and $\text{CO}+\text{CH}_4$, in continuous gas-flow reactor were carried out. The influence of the platinum distribution in the washcoat on the ignition and extinction processes for oxidation of CO on $\gamma\text{-Al}_2\text{O}_3$ and CeO_2 support was studied by CO-TPD experiments. The catalytic performance was compared for constant amounts of platinum and washcoat material for each sample. Low and high CO concentration were used (0.1 and 1% of the gas mix). Low-temperature activity

followed the order (from lowest to highest activity):



2.2.3. Task 2.2: Definition and preparation of reference catalysts

The reference catalyst is a current, commercially available, state of the art DOC. JM ref was prepared using a homogeneous formulation with 100g/ft³ total PGM and a ratio Pt/Pd=4/1.

All partners tested the reference catalyst and correlations studies were carried out for aging and test procedures. During the second year of the project CRF had at first focused the attention to the reference catalyst: both static light-off procedure and dynamic light-off test have been used for the characterization.

Catalysts were selected and ranked with respect to highest activity for oxidation of high concentrations of CO and HC at low temperatures.

2.2.4. Task 2.3: Laboratory tests on synthetic gas benches of selected new formulations

Determination of kinetic data for the prototype catalyst selected in order to implement these new data in exhaust system modelling tools in WP1. The selected new catalyst formulation and the reference catalyst provided by JM were tested in one of the synthetic gas bench reactor in Chalmers. Representative gas compositions were selected and kinetic data for CO and HC oxidation were determined. Comparison was made with the reference catalyst provided by JM. The tests were performed both with simplified and more complex gas compositions.

2.2.5. Task 2.4: Preparation of suitable sized monoliths for testing on a bench scale

Chalmers had synthesised and characterised two generations of model catalysts and also performed activity studies. They found an increase of activity for both CO and HC (CH₄ oxidation) performances when using ceria as a support instead of alumina. Scale up of catalysts powder from Chalmers University was done by JM. The coating procedure involved insuring that the coating has acceptable thermal shock resistance (quench test), acceptable mechanical shock resistance (high air velocity test), does not result in a finished catalyst with unacceptably high backpressure and does not cause significant deterioration of the properties of the monolith substrate. Synthetic gas bench testing was carried out to ensure JM material has the same priorities as the Chalmers catalyst powder. Two generations of DEV catalysts were benchmarked against the reference catalyst in JM and CRF using static and dynamic light-off conditions.

First generations of catalyst were prepared using Pt or Pt/Pd on ceria catalysts. Ceria support material supplied by Chalmers was pre-fired prior use for 2 hours at 600°C. Particle size distribution was checked prior to use in the slurry. Powder after thermal treatment was mixed with PGM salts and HC trap material to form the washcoat slurry and coated onto monolith substrates. For hot-spot preparation the PGM were added to a smaller portion of ceria material and the rest of the ceria was added after to reach the same final composition.

JM ref (Pt/Pd on alumina) was tested against newly developed Pt/Pd on ceria catalysts. Aging procedure was determined in collaboration with other partners. Catalysts were tested after hydrothermal stabilisation at 600°C/4hours and after HT aging at 800°C/24 hours. In order to improve data correlation and a better understanding of results observed with the different partners, test conditions optimisation/harmonisation were investigated (Chalmers, CRF, JM, PSA). The range of concentrations found by IFP with their HCCI calibration (i.e. CO concentration in the range 2000-4000 ppm, HC: 1600-2500 ppm) and the high methane content within the HC were taken in consideration in order to correctly evaluate the new catalytic formulations. HC mix according to IFP speciation using a molar ratio $C_3H_6/C_2H_4/CH_4=1/3/1$ was introduced (after discussions with CRF).

After optimisation of the test conditions it was observed in JM synthetic gas bench testing that ceria catalyst is clearly activated by high CO concentration compare to the alumina-based catalyst (JM ref). During their testing, CRF also observed very promising results for catalysts prepared with ceria but they suffered from rapid deactivation when testing in dynamic conditions.

This first generation of catalyst tested on synthetic gas bench in both JM and CRF laboratories displayed very promising results and confirmed previous results obtained by Chalmers University within Task 2.1. With light of these results, new formulations were developed around Chalmers formulation in order to obtain improved thermal stability, better adhesion of the washcoat while maintaining early light off in HCCI conditions. Formulations were benchmarked in JM and CRF against the reference catalyst:

- JM ref: Pt/Pd=4/1 @100g/ft³ on alumina + HC-adsorbent
- DEVA: Pt/Pd=4/1 @100g/ft³ on ceria + HC-adsorbent
- DEVE: Pt/Pd=4/1 @100g/ft³ on ceria + 20% alumina + HC-adsorbent
- DEVF: Pt/Pd=4/1 @100g/ft³ on ceria mixed oxide + HC-adsorbent
- DEVG: Pt/Pd=4/1 @100g/ft³ on ceria mixed oxide + 30% alumina + HC-adsorbent
- DEVG: Pt/Pd=4/1 @100g/ft³ on ceria mixed oxide + 50% alumina + HC-adsorbent
- DEVI: Pt/Pd=4/1 @100g/ft³ on ceria mixed oxide + 70% alumina + HC-adsorbent
- DEVJ: Pt/Pd=1/1 @100g/ft³ on ceria + 20% alumina + HC-adsorbent

DEVJ was developed trying to mimic hot spot formulation (Chalmers University Task 2.1) and using a ratio Pt/Pd=1/1 (higher palladium content for cost reduction and higher activity and thermal stability).

The alumina used as a binder is also there to improve PGM dispersion and stabilise the active phase of the catalyst. Very promising results were obtained when blending alumina with pure ceria material and using ceria mixed oxides components. Results obtained in JM synthetic gas bench showed that DEVJ has the best activity for CO light off after HT aging at 800°C for 24 hours. DEVE and DEVA also displayed good early light off properties but a decrease in performance was observed at higher temperatures (deactivation due to the modification of the ceria support). Similar trend was observed for HC light off. Overall under JM test protocol, DEVJ (layered catalyst) was found to be the best catalyst for CO and HC oxidation. Good results were also obtained with DEVG and DEVE before sulphation, however better performances were observed for DEVG after exposure to sulphur. After sulphation we also observed that performances for DEVJ catalyst were dramatically affected for both CO and HC performances. Desulphation studies were carried out in JM to determine which conditions should be used to recover clean activity. DEVJ and DEVG were selected by JM as being the best candidates for further studies within WP4.

Testing performed in CRF confirmed JM's results. DEVJ formulation shows the best catalytic performances among new formulations at stabilized condition (4h @ 600°C) and after hydrothermal aging at 800°C for 24 hours, especially for methane abatement. DEVJ catalytic performances are strongly decreased after CRF sulphur ageing procedure compare to DEVG that doesn't seem to be

influenced by the ageing methodologies used. The main reason has to be associated to sulphur that poison strongly catalysts with a lower Pt/Pd ratio (1:1 compared to 4:1 in DEVG).

During the scale up process it was necessary to utilize a large number of powder/slurry characterization techniques. Thermal and mechanical shock resistance of the coating was improved using colloidal ceria binder provided by Chalmers. Various in house rheology modifiers and binding agents were used to improve adhesion of the washcoat on the ceramic substrate. JM confirmed that material from Chalmers University and material used in production have the same properties. Specific surface area analysis and PGM dispersion were carried out to ensure that both coatings are as similar as possible.

Based on CRF and JM results, it was decided that DEVJ and DEVG were the best formulations for engine testing within WP4. New Pt/Pd advanced DOC technology shows very good performance to meet the extremely demanding HC/CO requirements but will require more demanding sulphur management. Backpressures were measured to ensure similar behaviour during engine testing. Engine test benches that will be performed inside WP4 will give further results and will give the final evaluation of the developed samples.

2.2.6. Task 2.5: Fundamental investigation of new catalysts formulation on the basis of specified secondary emissions from the plasma reactor from WP3

In order to achieve fundamental mechanistic data when exposed to plasma emissions, the selected new catalyst formulation and the reference catalysts were studied using both gas-flow reactor and *in situ* FTIR spectroscopy at Chalmers. Fundamental investigation (gas-flow reactor and spectroscopy experiments) on the role of the support material was also investigated. A parameter study focusing on the influence of NO₂ (model plasma molecule) and CO₂ (this was included as total oxidation of CO and CH₄ leads to CO₂ formation which may influence the role of the support) on the activity for oxidation of CO and CH₄ was carried out.

It was shown that NO₂ has a positive influence on the CO conversion below light-off temperature for alumina supported Pt catalysts. This was also observed by JM (Task 2.4) and should be carefully taken under consideration for testing with plasma device. Close to the light-off temperature, NO₂ seem to suppress the oxidation for the conventional catalyst (homogeneous Pt distribution) while for the hot-spot catalyst (heterogeneous Pt distribution) the influence was minor. CO₂ shows really minor influence on platinum alumina-based catalyst. The results show, in line with previous results (Task 2.3), that the hot-spot formulation more effectively converts CO at lower temperatures.

For ceria-supported catalyst, NO₂ has not the positive influence on CO conversion observed previously for alumina-based catalysts. For ceria supported Pt, CO₂ seem to have a negative effect on CO oxidation. Hot-spot catalysts displayed higher activity for CO oxidation in the presence of NO₂ and CO₂. Both NO₂ and CO₂ suppress the oxidation of CO over Pt/CeO₂ also for temperatures below light off suggesting that the active role (oxygen transport) of the support is influenced by the formation of nitrates and carbonates on the support. This indicates that the active role of the support may change such that the activity decreases.

2.2.7. Conclusion

We have shown during this project that catalyst performance can be significantly improved with the new developed formulation. Testing of the advanced DOC formulation show that increasing CO concentration will increase performances due to positive order kinetics of CO regarding platinum supported on ceria. Low temperature oxidation was improved while minimising in the same time the cost

of the DOC introducing larger amount of palladium in the catalyst formulation. Substituting platinum with palladium in DOCs results in precious metal cost saving and will improve thermal stability and performances in aged catalysts. The major challenge remaining of the advanced technology will be the high sensitivity to sulphur poisoning due to the use of ceria support and higher palladium content, but promising results were observed under certain desulphation conditions.

Newly developed technology showed a big improvement compare to standard commercial diesel oxidation catalyst. Improvement on sulphur tolerance and support material stability can be obtained by adapting support material (mixed oxide components), layering of the catalyst and modifying precious metal distributions within the layers of the catalyst. Engine rich purges can be implemented in order to recover activity after sulphation and low sulphur fuel introduction will contribute to maintain high activity at low temperature. This project has proved that lowering emission pollutants can be achieved only with active collaboration between engine designs, high quality fuels and advanced emissions controls strategies.

2.3. WP3: Emerging flexible low temperature oxidation technologies

2.3.1. Introduction

A major element of work package WP3 was the incorporation of plasma technology into a diesel engine exhaust line. The work on this subject which was accomplished over the three year period took place on three different experimental levels and at three different corresponding locales. The three different experimental scales were laboratory-scale, synthetic gas bench (SGB)-scale, and engine test bench-scale, and were performed at Supelec, PSA-Velizy, and IFP-Lyon, respectively. Electrical system design and construction for support of the experimental work on the SGB and engine test bench work was also done at Supelec.

The smaller, laboratory-scale work occurred at Supelec over the entire project duration. Laboratory work began on a quite simple level, investigating the effects of plasma treatment of naphthalene, which was considered as a model compound for the heavier hydrocarbons among the various species found in diesel exhaust. While as the project progressed and this choice of compound was found to be less than extremely pertinent, the experimental work produced some interesting results and led to a publication in an international peer-reviewed conference proceedings¹. The next steps of laboratory work concerned the treatment of both carbon monoxide and methane by both plasma and combined plasma-catalyst processes. This work would lead to some of the most interesting advances on plasma-catalyst interaction in the project including the idea for the alternative process of ozone injection upstream of the catalyst. The work on methane treatment by plasma was also published in a peer-reviewed journal article².

The next two stages of work were done at the PSA and IFP laboratories. The idea for ozone injection, which was developed based on some of the laboratory level experiments, was also tested on both the SGB at PSA and on the engine test bench at IFP.

¹ Mfopara, A., Kirkpatrick, M.J., Odic, E., "Oxidation of a model PAH and its solid by-products by atmospheric pressure dielectric barrier discharge," conference proceedings of the International Symposium on Non-Thermal Plasma Science and Technology-6 (ISNTPT-6) (2008).

² Mfopara, A., Kirkpatrick, M.J., Odic, E., "Dilute methane treatment by atmospheric pressure dielectric barrier discharge: effects of water vapor," Plasma Chem Plasma Process, (2009) 29:91-102. DOI 10.1007/s11090-008-9164-9.

2.3.2. Laboratory-scale

2.3.2.1. *Preliminary Experiments - PAH (polyaromatic hydrocarbon) treatment*

The major findings of this study were that naphthalene can be relatively easily removed from the gas phase by non-thermal plasma treatment (90% removal from gas phase with a 50J/L energy cost for a 50 ppm naphthalene inlet concentration). Gas phase oxidation by-products are CO₂ (major), CO and very small amounts (less than 5 ppm) of phthalic anhydride and naphthoquinone. But the naphthalene oxidation by the process was not complete, and led to the formation of a solid byproduct which was deposited on the reactor walls. This deposit can in turn be oxidized by the plasma into primarily CO₂, however on a different time scale from the fast treatment of gas phase naphthalene. This result may be interpreted to mean that the plasma process could be useful for an automotive application to take advantage of this phase change of the initial pollutant, obtained at moderate energy cost, to “store” the material to then be treated afterward by advanced oxidation of the solid by-product by the plasma and/or catalysis during the complete cycle.

2.3.2.2. *Preliminary Experiments - Methane conversion and effect of water vapor*

In the early stages of the PAGODE project, methane was identified as a serious problem compound for diesel oxidation catalysts. The question inevitably came up as to whether plasma technology might be of assistance specifically with regard to methane treatment. Therefore, a series of laboratory-scale experiments were conducted at Supelec in order to get a general idea of the potential of plasma technology to address this issue, even though it is generally known that methane is one of the more difficult compounds to degrade. The experiments bore out the initial assumption that plasma treatment of methane would be far too energy inefficient to be cost effective. Nevertheless, it is worthy of note that the addition of water vapour to the gas increased methane conversion and that nothing necessarily precludes the possibility that with some as yet unknown catalyst, that a “synergistic” effect between plasma and catalyst treatment could be found as was indeed the case with carbon monoxide as discussed in the following sections.

2.3.2.3. *Preliminary Experiments - Combined plasma-catalyst treatment of carbon monoxide*

Laboratory-scale experiments performed at Supelec on the interaction between the plasma-treated gas with a diesel oxidation catalyst placed just downstream of the plasma reactor showed the potential for a synergistic effect between two processes for the oxidation of carbon monoxide (see Figure 7): plasma only treatment of 1000 ppm CO led to 8% CO removal (oxidation); catalyst only treatment of 900 ppm CO led to 11% CO removal (storage/oxidation), whereas a 78-91% removal (oxidation) of CO was observed with the plasma-catalyst combination treatment. Interpretation of the experiments tentatively indicated that the effect could be due to a heterogeneous reaction between ozone and carbon monoxide (see DOC temperature increase when ozone is added in Figure 7), which led directly to the idea of ozone injection in the exhaust gas line. The idea for ozone injection is based both on the experimental evidence for a synergistic effect and the practical consideration of significant reductions in both capital and operating costs related to the plasma reactor itself.

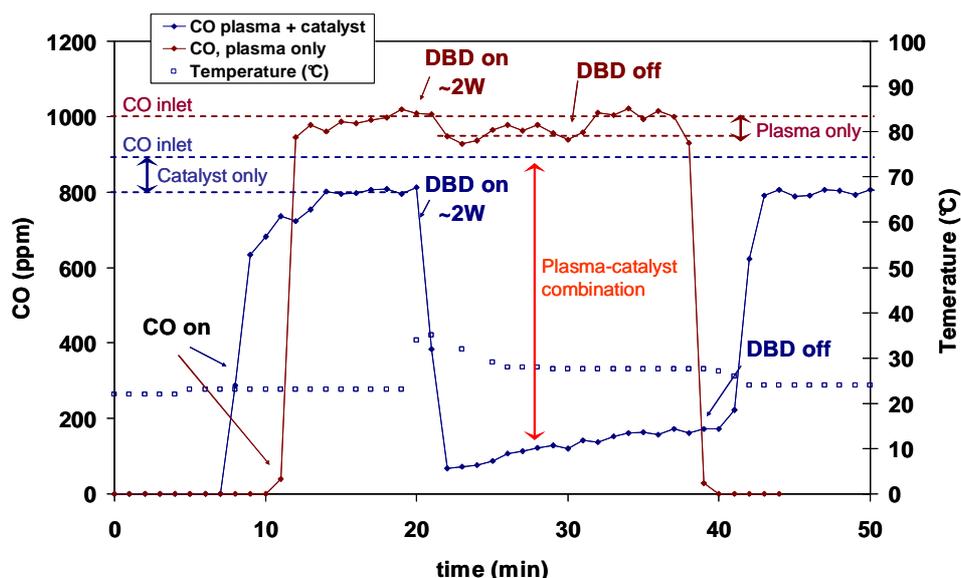


Figure 7. Laboratory scale plasma-catalyst treatment of CO (900 ppm CO inlet concentration in synthetic air, 2 L/min - room temperature, non-thermal plasma input power: 2 W – ON/OFF experiment)

2.3.3. Synthetic gas bench

2.3.3.1. Synthetic gas bench - In-line plasma-catalyst experiments

A series of experiments were performed using the PSA synthetic gas bench and the bench-scale plasma system which was designed and built at Supelec. In general, the results of these experiments showed that the plasma had a positive effect on the performance of the catalyst, leading to a reduction in the light-off temperature for both carbon monoxide and unburned hydrocarbons (see Figure 8). However, for the gas flow rate used in these experiments, the energy cost was relatively high (120J/L in Figure 8), leading to doubts about whether this technique would prove to be as energy efficient as necessary when tested on the engine test bench at IFP. This observation coupled with the results of the laboratory-scale experiments which suggested that a significant enhancement of carbon monoxide removal by the system could be simply explained by a heterogeneous reaction with ozone, led to the decision to try the alternative approach of ozone injection on the synthetic gas bench in addition to the already planned so-called “in-line” combined plasma-catalyst experiments.

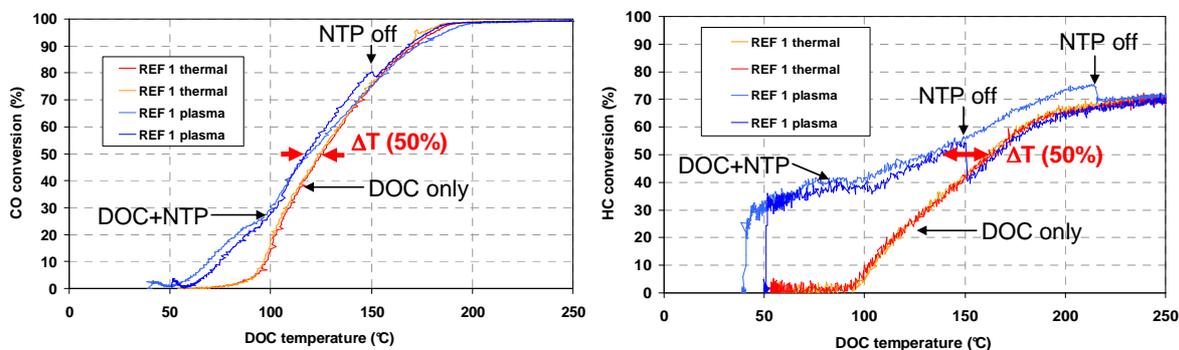


Figure 8. SGB – in-line combined plasma catalyst experiments. Carbon monoxide HC light-off curves with (blue curves) and without plasma (red curves). Catalyst: REF1. NTP energy cost: 120J/L

2.3.3.2. Synthetic gas bench - Ozone injection experiments

The potential advantages of the approach of ozone injection from a practical point of view (without regard to possible enhanced performance over the in-line plasma approach) are related to a reduction in the size of both the plasma reactor itself and its attendant power supply. In addition to the standard temperature light-off tests, which were analogous to the in-line plasma experiments, several experiments were also performed in order to better understand some confusing results involving nitrogen oxides. Overall, the results of this series of tests gave results which were comparable to the in-line plasma tests, but with significantly reduced energy costs (26-80J/L in figures 9 and 10) in addition to the practical advantages mentioned before. Figures 9 and 10 illustrate the effect of ozone injection on both CO and hydrocarbons emissions, respectively. The figures show time course data for species concentration for both thermal only and ozone injection experiments and for three different levels of power used for the generation of ozone. Ozone injection begins shortly after the beginning of the experiments, and is followed by a ramp in temperature of the catalyst (REF), the effect of which is seen in the “thermal only” (red) curves. As can be seen, the injection of ozone significantly reduced both carbon monoxide and hydrocarbon concentrations, albeit in a somewhat transient fashion, especially for the case of carbon monoxide.

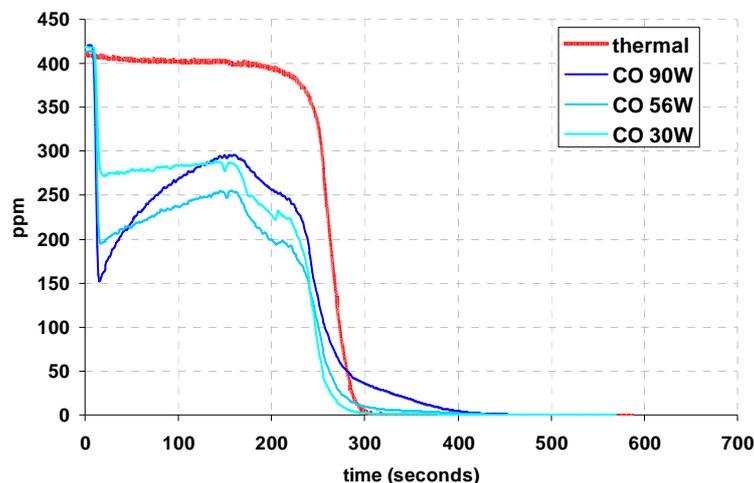


Figure 9. SGB – ozone injection experiments. Carbon monoxide concentration as a function of time for different levels of power used for ozone generation (blue curves) and without ozone injection (red curve). Catalyst: REF1. NTP energy cost: 26-80J/L. Temperature ramp beginning at 50°C started at 180 s experimental time

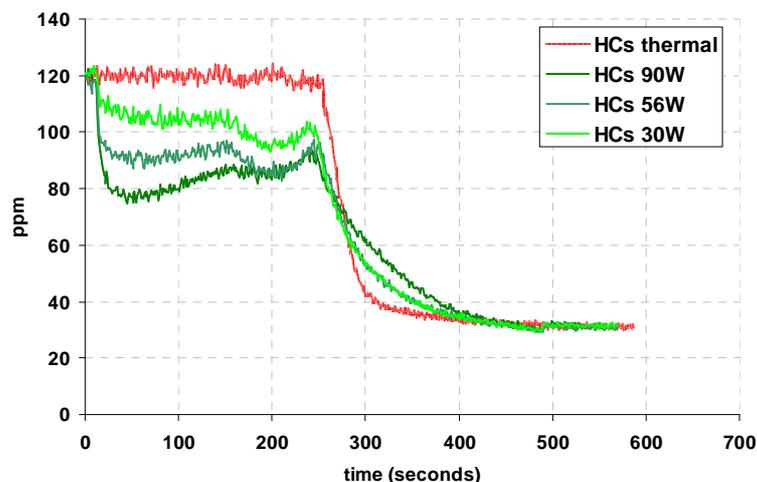


Figure 10. SGB – ozone injection experiments. Hydrocarbon concentration as a function of time for different levels of power used for ozone generation (green curves) and without ozone injection (red curve). Catalyst: REF1. NTP energy cost: 26-80J/L. Temperature ramp beginning at 50°C started at 180s experimental time

2.3.4. Engine test bench

The electrical discharges group from Supelec took part in experiments which were performed on the engine test bench at IFP, Lyon. Both the in-line plasma and ozone injection type of experiments which had been tested on the synthetic gas bench at PSA were thus translated to a third experimental scale, that being an actual diesel engine. It should be mentioned that maximum energy costs were evaluated at idle for both configurations: 45J/L for in-line combined plasma catalyst and 34 J/L for ozone injection. These experiments were performed in the cadre of work package 4 (see section 2.4. WP4).

2.3.5. Conclusions and perspectives

Over the three-year period of the PAGODE project, significant progress was made over three different experimental scales on the subject of the emergent technology of plasma treatment of diesel exhaust gas coupled with oxidation catalysts. Two different ideas were tested on all three experimental scales, that of in-line plasma treatment of the gas upstream of the catalyst and then of ozone injection upstream of the catalyst. The idea for ozone injection upstream of the catalyst came about because of early laboratory-scale experiments as well as disappointing results in terms of the energy efficiency of the enhancement of catalyst performance by the in-line plasma treatment upstream up the catalyst on both the synthetic gas bench and engine test bench scales. In-line treatment of diesel exhaust gas upstream of a catalyst has been shown to have serious energy efficiency issues, combined with the need for a robust (expensive) ceramic-coated plasma reactor. Ozone injection addresses both of these issues, but its testing in the PAGODE project was exploratory and therefore not complete. Therefore, while plasma technology has been found to be lacking in certain aspects for this application, an alternative emergent technology has been identified and tested, and so further research and investigation is warranted.

2.4. WP4: System synthesis for next powertrain generation

2.4.1. Introduction

WP4 is the latest PAGODE work package. The objective was to evaluate and optimize the newly developed concepts such as catalytic formulations and plasma reactor on the HCCI engine. Initially, ozonizer tests were not planned. However, regarding the potential identified during WP3, a full-scale ozonizer was also tested on the HCCI engine coupled with selected DOC formulations.

2.4.2. Catalyst prototypes evaluation

Additionally to the reference catalyst REF, the selected catalytic formulations developed during WP2 were DEV G and DEV J according to their better performance from SGBT:

- REF: 100 g/ft³ - Pt/Pd = 4/1 - Alumina + HC-adsorber
- DEVG : 100 g/ft³ - Pt/Pd = 4/1 - Ceria-zirconia + Alumina (30%) + HC-adsorber
- DEVJ : 100 g/ft³ - Pt/Pd = 1/1 - Layered - Ceria + Alumina (20%) + HC-adsorber

The total PGM mass was set constant for all formulations. DEVG formulation included a ceria-zirconia support with 30% of alumina, whereas DEVJ formulation was developed trying to mimic hot spot formulation and using a ratio Pt/Pd=1/1. Catalysts were tested after aging protocol performed by Johnson Matthey:

- Hydrothermal conditions 24h @ 800°C in oven

- Stabilization 1h @ 650°C on the engine test bench

From both steady state and transient tests (engine speed and torque ramp), it can be concluded that DEVJ catalyst presents the best behavior regarding both light-off and extinction temperature for both CO and HC as well as storage capability at low temperature. These results are in line with those obtained during WP2 from SGTB and are explained by the presence of Ceria which has a high O₂ storage capability and by the hot spot effect created by the layered coating. Furthermore, the lower Platinum amount for DEVJ catalyst allows about 25% cost saving compared to REF catalyst.

It appears that methane remained difficult to treat, even with advanced formulations. None of the catalysts is able to treat below 460°C. So, as it is well known, methane oxidation at low temperature remains challenging.

2.4.3. Plasma assistance evaluation

Effect of the NTP reactor on the exhaust gas was evaluated in both idle and 1500 rpm / 2 bar BMEP steady state running conditions, that is for the lowest exhaust gas temperature levels. The results were quite similar whatever the catalyst formulation (REF or DEVJ).

From the HC point of view, the DOC alone is very efficient at low temperature owing to the HC trap material and the additional effect of the NTP is therefore very limited (2-3 %). From detailed results analysis, we saw that positive NTP effect on HC appears mainly when the amount of HC trapped within the DOC is low. On the contrary, for higher level of HC trapped within the DOC, the NTP enhanced the undesirable desorption phenomena.

Since the catalyst is not lit-off (100°C at idle and 180°C at 1500 rpm - 2 bar BMEP), no CO conversion efficiency for DOC alone is measured. When the NTP is powered, a CO conversion efficiency of about 20% at 1500 rpm/2 bar BMEP can be observed. However, this effect seems to be mainly caused by the thermal effect of the NTP which increases the inlet DOC temperature enough to get catalytic reactions.

If a very limited positive effect on HC and CO can be observed, a negative effect related to NO_x emissions was identified; about 50 % increase at both idle and 1500/2. The relative NO_x increase is significant because of the very low absolute level of NO_x (~ 5-30 ppm) from the HCCI combustion mode. The following reactions mechanism can explain the NO_x emissions promoted by the plasma:

- $N_2 + e^- \rightarrow 2 N \cdot + e^-$ (N₂ molecular dissociation by the electron energy)
- $N \cdot + O \cdot \rightarrow NO$
- $NO + O \cdot \rightarrow NO_2$
- $N_2 + O \cdot \rightarrow NO + N \cdot$

In addition to steady state tests, transient light off tests were done and no significant positive effect from NTP could be observed (HC storage efficiency was a little better).

A few tests without any DOC downstream of the NTP were performed. In this configuration, an HC reduction of about 10% can be observed. On the contrary, there is no effect on CO. This result tends to prove an antagonism phenomenon between gas phase reactions within the plasma and catalytic reactions within the DOC depending on the reactant, HC or CO. Regarding NO_x, the plasma alone increase the NO_x formation similarly to the configuration with DOC.

2.4.4. Ozonizer assistance evaluation

Ozonizer evaluation was not initially planned within the PAGODE project. However, from the results obtained on SGTB during WP3, it was agreed between the partners to perform some tests on the engine. Thus, this was more a first rapid evaluation to confirm the potential discovered during WP3 than a more complete characterisation as done for the NTP.

For these tests, the ozonizer was fed with pure oxygen to enhance the ozone formation. The power supply was 370 W, that is 25% less than for the NTP. This setting gave an estimated ozone concentration in oxygen of 1.2% vol. From Supelec lab-measurements, the estimated ozone concentration was around 380 ppm at idle and 235 ppm at 1500 rpm – 2 bar BMEP running conditions by assuming that there is no ozone thermal destruction from the ozonizer to the DOC.

The maximum effect of the ozonizer was observed at idle, probably because of the higher ozone concentration and the lower temperature. Like for the NTP, the additional conversion efficiency is weak for HC (DOC alone is very efficient). Regarding CO conversion efficiency, it reaches 20%, which is a little bit better. Contrary to the NTP, a positive effect on NO_x was observed with about 50% NO_x reduction (inlet level ~ 5-30 ppm). The impact of ozone injection is more limited at 1500 rpm - 2 bar. The pollutant reduction is only 10% for CO and 25% for NO_x. To better understand the phenomena, some tests without any DOC were done. They show the same tendency for NO_x, meaning that gas phase reactions occur within the NO_x reduction mechanism.

These results are in line with those obtained during WP3. However, the tested configuration was a prototype one. For example, oxygen as feed gas cannot be considered on a vehicle. Furthermore, ozone was not measured at DOC outlet. Since it is a very active reactant, we can imagine that it is fully consumed, but this point must be validated.

2.4.5. NMVEG and ARTEMIS cycles simulation

As a final part of WP4 activities, a validation of the system developed inside PAGODE framework was carried out via simulation activities covering the NMVEG cycle and ARTEMIS cycle by both PSA and CRF using experimental data from IFP engine test results.

Since PSA and CRF simulation approaches and hypotheses are different, especially concerning the warm up phase of the cycle during which the catalyst is not active yet and the engine coolant temperature remains cold, it is more difficult to compare the data from an absolute point of view. However, the same tendency is observed. Compared to the REF catalyst, DEVJ catalyst gives the best results. About 15-20% less HC and 20% less CO emissions at tail pipe can be observed. On the contrary, the DEVG catalyst seems to be worse than the REF catalyst.

Regarding absolute value, both HC and CO emission levels are significantly higher than EURO 6 emission limits. This can be explained by two aspects. The first one is related to engine out emission level which is high, up to 0.4 - 0.5%. The second one is related to exhaust gas temperature level which remains below 250°C during a very long period of the cycle. Since the light-off temperature (calculated from brick inlet temperature) of the catalysts is around this value, DOC efficiency remains too low, showing that optimisation work is needed to further reduce catalyst light-off temperature.

2.4.6. Guidelines for further developments

HCCI combustion

The NADI™ concept used during the project is now an old one, with high CO and HC emissions, close to 0.5%. For a future development approach of PAGODE concept a new optimised³ HCCI combustion system will be required, taking into account biodiesel fuels and oxidation catalyst enhanced capabilities at low temperature; CO and HC emissions have to decrease by an order of magnitude to be treated by a Non Thermal Plasma reactor and an oxidation catalyst with acceptable Platinum and Palladium loadings.

DOC

Despite highly promising results observed with the new developed formulation, we have seen that low-temperature oxidation activity still remains very challenging during HCCI combustion mode.

During the development of the low temperature oxidation formulations we have focussed our attention on the influence of the support material (introduction of ceria) and of the precious metal (distribution, metal loading, Pt:Pd ratio). We have seen a great improvement using platinum-palladium catalyst supported on ceria type material (high oxygen storage component). The distribution of the precious metal was also studied and extra benefit was obtained using "hot spot" formulation (heterogeneous distribution of the precious metal within the support).

Further work should be carried out in this direction in order to improve further cold start performances. Support material composition can be optimised to offer better precious metal distribution and greater thermal and sulphur stability (mixed oxide components, ratio ceria:alumina, surface area). Metal loading, Pt:Pd ratio and metal zoning (both horizontal and vertical) need to be carefully investigated, in relation to CO and HC emissions and flow rate conditions, to enhance the catalyst performances. Finally, replacing platinum or adding gold in the catalyst formulation has shown recently some very promising results and constitutes one of the main ways forward for low temperature oxidation. It is well known that gold exhibits high activity at low temperature but only when deposited in nanoparticles form on base transition metals.

Catalytic activity can therefore be improved further via fine-tuning of the catalyst washcoat composition in order to get the most out of the active phase of the catalyst in these specific exhaust gas and temperatures conditions.

NTP

Regarding NTP, even if limited from absolute level, the NO_x increase remains an issue. Furthermore, electric consumption must be reduced to limit the over fuel consumption and associated CO₂ emissions. Since two failures occurred during the test period, durability must be improved.

Ozonizer

The future ozonizer system for an on-board vehicle application should reach the optimal efficiency (100 g/kW.h) with feed air. It also should be able to minimize NO_x formation by limiting the warm-up generated by the discharge. This objective could be reached by generating surface discharges on an insulated material. Ideally, this material could be flexible (polymer for example) in order to be compatible with vibration requirement. Durability of such a material under an electrical discharge remains to be demonstrated. Furthermore, the lack of by-products emissions as ozone, N₂O... outlet DOC must be validated.

³ Guillaume Bresson et al., "A Study of Methods to Lower HC and CO Emissions in Diesel HCCI", SAE paper 2008-01-0034, 2008.

2.4.7. Conclusions

During the work package 4, two prototype DOC formulations were tested on an HCCI engine (NADI™ concept) and compared to the Euro 4 reference formulation (REF). The formulation called DEVJ, based on Ceria support and layered coating, offered the best performances with the highest HC storage capability and the lowest light-off temperature regarding HC and CO. It was also the only active formulation regarding CO at low temperature, especially in transient conditions. Driving cycle simulation work confirmed the better efficiency of this new formulation. Furthermore, this new formulation contains the lowest platinum quantity, leading to the lowest cost. Nevertheless, no improvement was found regarding methane conversion, which remains challenging.

The full-size NTP reactor showed a quite limited positive assistance effect. Only a very small additional effect on HC was observed and this one tended to be far less efficient than DOC HC storage effect. The impact was higher on CO, with a maximum conversion comprised between 10 and 25%. As a side effect, the plasma activation led to a significant NO_x increase. Moreover, such a NTP reactor in the exhaust line remains fragile: two failures were encountered during the test phase. Due to the relatively high power requirement (500 W), the estimated fuel consumption penalty is estimated about 3% and remains an issue.

Regarding the full-size ozonizer device, additional effect on HC and CO appeared mainly at very low temperature, with better results than for the NTP at idle. Furthermore, the ozonizer showed a better potential regarding NO_x, although 25% power less was consumed. About 50% NO_x reduction efficiency was observed (low absolute NO_x level ranging from 5 to 30 ppm). The reaction mechanism for NO_x reduction is not clear yet and further research work is necessary to better understand both gas and catalytic phase reactions. However, several key points remain to be solved such as ozone production efficiency with air as feed gas (only oxygen was tested during the tests), electric consumption to limit fuel consumption penalty, packaging, durability, cost... The temperature efficiency window has to be identified and the absence of by-products emissions like ozone, N₂O must also be validated.

For a future development approach of PAGODE concept, new optimised HCCI combustion systems will be also required, taking into account bio diesel fuels and oxidation catalyst enhanced capabilities at low temperature; CO and HC emissions have to decrease by an order of magnitude to be treated by a Non Thermal Plasma reactor or an ozonizer and an oxidation catalyst with acceptable Platinum and Palladium loadings and a lower light-off temperature.

3. Dissemination and Use

The results of PAGODE will help automobile industry to develop affordable innovative technical solutions dedicated to the future Diesel engine.

PAGODE is the place where complementary skills are joining their efforts to answer technological challenges on the after treatment of the next generation of Diesel engine.

All the scientific information released by the PAGODE project is available for all the project partners. Public scientific papers were encouraged and presented either in journals or international conferences (see list below) in order to ensure a wider diffusion of the results. The dissemination of proprietary, key technological results were specifically discussed in the steering group committee during the project, in

order to ensure that industries and organizations investing in research keep an advantage over those who do not.

Presentation of the project was encouraged in order to ensure that the community is aware of the vision and development work carried out in PAGODE.

Communications

- EUCAR Conference 2006, November 22-23, 2006 at Brussels (Belgium): poster
- EUCAR: The Fuels and Powertrain Program Board, June 15, 2007 at Brussels (Belgium): presentation
- EUCAR Conference 2007, November 8, 2007 at Brussels (Belgium): poster
- Transport Research Arena Europe 2008, April 21-24, 2008 at Ljubljana (Slovenia): presentation
- 6th Intern. Symp. on Non-Thermal Plasma Technol., May 12-16, 2008 at Taipei (Taiwan): presentation
- SAE Powertrains, Fuels & Lubricants congress, June 23-25, 2008 at Shanghai (China): presentation
- 6th conf. SFE2008, July 7-9, 2008 at Gif-sur-Yvette (France): presentation
- EUCAR Conference 2008, November 26, 2008 at Brussels (Belgium): poster and presentation
- EUCAR: The Fuels and Powertrain Program Board⁴, May 5-6, 2009 at Brussels (Belgium): presentation
- EUCAR Conference 2009, November 9-10, 2009 at Brussels (Belgium): poster

Publications

- A. Mfopara, M.J. Kirkpatrick, E. Odic "Oxidation of a model PAH and its solid by-products by atmospheric pressure dielectric barrier discharge", Proc. 6th Intern. Symp. on Non-Thermal Plasma Technol., Taipei-Taiwan, 12-16 May 2008, 6 p.
- S. Zinola, J. Lavy, A. Jaecker-Voirol "Towards CO and HC aftertreatment devices for the next generation of Diesel engines", SAE Powertrains, Fuels & Lubricants congress in Shanghai, June 2008.
- A. Mfopara, M.J. Kirkpatrick, E. Odic "Methane oxidation by atmospheric pressure dielectric barrier discharge: effects of water vapor", Proc. 6th conf. SFE2008, Supelec-France, 7-9 July 2008, 372-376.
- A. Mfopara, M.J. Kirkpatrick, E. Odic, "Dilute Methane Treatment by Atmospheric Pressure Dielectric Barrier Discharge: Effects of Water Vapor", Plasma Chem Plasma Process (2009), 29:91-102.
- A. Mfopara, "Etude de l'oxydation par décharges électriques à pression atmosphérique de deux molécules modèles en vue d'une application au traitement d'effluent automobile : le naphtalène et le méthane." Thesis at Pierre and Marie Curie University (19 March 2009).

4. Project Conclusion

Diesel Homogeneous Charge Compression Ignition (HCCI) combustion processes are seen as a promising way to meet future environmental challenges, which will have to achieve both significantly lower pollutants emissions and fuel consumption. With these concepts, NO_x and PM emissions are simultaneously and drastically reduced while avoiding the installation of a complex and costly NO_x

⁴ Due to very stringent restrictions on travel which were being imposed at that time, several Project Coordinators could not ensure their participation at the Fuels and Powertrain Program Board meeting on 5 – 6 May 2009. Therefore the Fuels and Powertrain Program Board meeting was postpone, the Project Coordinators sent their Project's presentation, which were put on the EUCAR extranet (available for all the EUCAR Fuels and Powertrain Program Board Members).

specific after treatment system. However, HC and CO emissions from HCCI combustion mode are significantly increased and PAGODE project provided a comprehensive system by coupling a Non Thermal Plasma (NTP) reactor with a specific oxidation catalyst for CO and HC abatement.

IFP carried out Renault engine modification for the HCCI combustion capability. This adaptation includes a reduction of the compression ratio from 17.7:1 to 14:1 with a dedicated piston chamber based on NADI™ concept, a narrow injector cone angle realized in accordance with pistons chamber and a reduction of the swirl number. A high permeability and high cooling efficiently prototype EGR circuit has been also carried out.

HCCI operating points calibration activities was carried out according to the state-of-the-art strategies developed at IFP. In total, six operating points have been successfully calibrated with respect of pollutant limits.

Globally, HCCI does not significantly modify the exhaust gas temperature level compared to Euro 4 combustion. This result was expected from bibliographic study and confirmed by CRF data. It may be considered as a very positive result regarding the after-treatment issue.

In HCCI mode, CO and HC emissions show wide raise compared to conventional mode. The experimental data as well as data collected from CRF internal activities show an increase factor of 2-3 in the case of CO and up to a factor 4-5 in the case of hydrocarbons.

On the other hand, NO_x emission in HCCI mode is about the half compared to conventional mode and the PM emission reduction can be estimated even up to one order of magnitude.

Concerning the fuel consumption, results obtained under HCCI combustion are very close to those obtained in conventional combustion.

Detailed analysis of exhaust emissions has been done. The engine-out results shows that the HC repartition is quite similar in HCCI and in Euro 4 combustion, including HC in the C1-C9 range, aldehydes and ketones. However, as the absolute level of HC is higher at HCCI engine-out, the absolute level of each species is also higher.

An Euro 4 oxidation catalyst has been tested in order to evaluate strong and weak points of the current technology and selected as a reference for the following PAGODE tasks. Tests show that pollutant emissions are efficiently converted by the catalyst when active, including harmful emissions of benzene, 1,3-butadiene and formaldehydes. At idle, the temperature is too low and no pollutant species can be treated. The tests have also shown that there is mainly methane remaining after DOC. This pollutant is particularly hard to treat with classical formulation. From our tests, only 10% has been successfully converted at 470°C. Therefore it is necessary to improve both the light-off performance of the catalyst and the methane oxidation efficiency to comply with the future standards.

With B10 fuel, NO_x, HC and CO emissions are slightly lower than with standard fuel, while PM emissions are slightly higher.

This preliminary study provided boundary data for the development of innovative modelling software tools, for the design of suitable catalyst regarding HCCI emissions (WP2) and for the development of the advanced technique of non-thermal plasma (WP3).

A fully 2-D / 3-D simulation tool for the DOC within the exhaust line was successfully developed. An initial single channel DOC model was extended in its formulation and implemented as an embedded module in a widely available CFD solver with requisite user-interface facilities, allowing the wider use of the tool within the consortium.

The assessment of the simulation tool was firstly carried out comparing experimental results coming from SGB testing rig. Relating to the first testing protocol, important differences between simulated and experimental results were noticed, while good accordance could be seen if the comparison was made relating to second testing protocol (in particular at aged conditions). Such good accordance could be highlighted not only in terms of T50 light-off, but also in the conversion efficiency trend all along the investigated temperature.

The assessment of the simulation tool against transient test bench data showed the overall capability and utility of the tool for DOC investigation under transient HCCI-like exhaust conditions. The $\pm 10\%$ cumulative emissions accuracy target was met for a number of the transient responses. However, novel formulations such as DEVJ necessitate the addition of CO buffering phenomena to the DOC model as they play a major role in low temperature CO abatement response.

We have shown during this project that catalyst performance can be significantly improved with the new developed formulation. Testing of the advanced DOC formulation show that increasing CO concentration will increase performances due to positive order kinetics of CO regarding platinum supported on ceria.

Low temperature oxidation was improved while minimising in the same time the cost of the DOC introducing larger amount of palladium in the catalyst formulation. Substituting platinum with palladium in DOCs results in precious metal cost saving and will improve thermal stability and performances in aged catalysts. The major challenge remaining of the advanced technology will be the high sensitivity to sulphur poisoning due to the use of ceria support and higher palladium content, but promising results were observed under certain desulphation conditions.

Newly developed technology showed a big improvement compare to standard commercial diesel oxidation catalyst. Improvement on sulphur tolerance and support material stability can be obtained by adapting support material (mixed oxide components), layering of the catalyst and modifying precious metal distributions within the layers of the catalyst. Engine rich purges can be implemented in order to recover activity after sulphation and low sulphur fuel introduction will contribute to maintain high activity at low temperature. This project has proved that lowering emission pollutants can be achieved only with active collaboration between engine designs, high quality fuels and advanced emissions controls strategies.

Over the three-year period of the PAGODE project, significant progress was made over three different experimental scales on the subject of the emergent technology of plasma treatment of diesel exhaust gas coupled with oxidation catalysts. Two different ideas were tested on all three experimental scales, that of in-line plasma treatment of the gas upstream of the catalyst and then of ozone injection upstream of the catalyst. The idea for ozone injection upstream of the catalyst came about because of early laboratory-scale experiments as well as disappointing results in terms of the energy efficiency of the enhancement of catalyst performance by the in-line plasma treatment upstream up the catalyst on both the synthetic gas bench and engine test bench scales. In-line treatment of diesel exhaust gas upstream of a catalyst has been shown to have serious energy efficiency issues, combined with the need for a robust (expensive) ceramic-coated plasma reactor. Ozone injection addresses both of these issues, but its testing in the PAGODE project was exploratory and therefore not complete. Therefore, while plasma technology has been found to be lacking in certain aspects for this application, an alternative emergent technology has been identified and tested, and so further research and investigation is warranted.

Two prototype DOC formulations were tested on an HCCI engine (NADI™ concept) and compared to the Euro 4 reference formulation (REF). The formulation called DEVJ, based on Ceria support and layered coating, offered the best performances with the highest HC storage capability and the lowest light-off temperature regarding HC and CO. It was also the only active formulation regarding CO at low temperature, especially in transient conditions. Driving cycle simulation work confirmed the better efficiency of this new formulation. Furthermore, this new formulation contains the lowest platinum quantity, leading to the lowest cost. Nevertheless, no improvement was found regarding methane conversion, which remains challenging.

The full-size NTP reactor showed a quite limited positive assistance effect. Only a very small additional effect on HC was observed and this one tended to be far less efficient than DOC HC storage effect. The impact was higher on CO, with a maximum conversion comprised between 10 and 25%. As a side effect, the plasma activation led to a significant NO_x increase. Moreover, such a NTP reactor in the

exhaust line remains fragile: two failures were encountered during the test phase. Due to the relatively high power requirement (500 W), the estimated fuel consumption penalty is estimated about 3% and remains an issue.

Regarding the full-size ozonizer device, additional effect on HC and CO appeared mainly at very low temperature, with better results than for the NTP at idle. Furthermore, the ozonizer showed a better potential regarding NO_x, although 25% power less was consumed. About 50% NO_x reduction efficiency was observed (low absolute NO_x level ranging from 5 to 30 ppm). The reaction mechanism for NO_x reduction is not clear yet and further research work is necessary to better understand both gas and catalytic phase reactions. However, several key points remain to be solved such as ozone production efficiency with air as feed gas (only oxygen was tested during the tests), electric consumption to limit fuel consumption penalty, packaging, durability, cost... The temperature efficiency window has to be identified and the absence of by-products emissions like ozone, N₂O must also be validated.

For a future development approach of PAGODE concept, new optimised HCCI combustion systems will be also required, taking into account bio diesel fuels and oxidation catalyst enhanced capabilities at low temperature; CO and HC emissions have to decrease by an order of magnitude to be treated by a Non Thermal Plasma reactor or an ozonizer and an oxidation catalyst with acceptable Platinum and Palladium loadings and a lower light-off temperature.