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Effect of Oil Consumption over an Innovative Exhaust After-Treatment System Suitable For Cogeneration Plants

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Abstract – In the following Paper, the behaviour of an innovative exhaust after-treatment system, suitable for internal combustion engines (ICE) powerplants working at stoichiometric conditions, is discussed in respect to its resistance to oil and ash contamination. This system is based on an unconventional double-stage system made up of a first oxidative filter followed by a three-way catalyst, which has been constructed, developed and tested at STEMS-CNR (the Italian National Research Council). The prototype has shown very interesting performances in terms of overall reduction of exhaust emissions even after a long exposure to lubricant contamination, maintaining a high efficiency during all its lifetime. Moreover, the effective service of this solution resulted prolonged if compared to standard after-treatment systems such a conventional three-way catalyst, as the latter greatly suffers the presence of partially burned oil produced by engines at the escape, especially after a very long running period. Catalyst failure is very common in ICE cogenerative and distributed plants making this prototype an important means to reduce emissions during the entire lifespan of cogenerative and distributed generation systems, which will be soon applied into smart-grids as energetic support of residential units and as recharger for electric vehicles.

***Keywords*:** Internal Combustion Engine, gas after-treatment, catalyst, particle filters, cogeneration units

1. Introduction

It is well known that normal oil consumption in an internal combustion engine can negatively affect the right functioning of the three-way catalyst (TWC, from now on) after a long running period, thus determining a significant increase of gaseous emissions [1-3]. This aspect is well verified in the typical case of distributed generating plants or cogenerative systems, which could be the base of several energy arrangements, such as a smart-grid or micro-grids, in a near future. Most of these generation units are based on Heavy-Duty engines, then converted to stoichiometric spark ignition engines, and are provided with a TWC, whose overall efficiency seems to be mainly affected by the onset of surface deactivation/poisoning phenomena due to the post-combustion ash deposit of the lubricant inside the engine. Indeed, the deactivation/poisoning of the catalyst appears even more important than the one related to thermal deactivation, being the running temperatures relatively low even in case of straight stoichiometric combustion. The main reason for which the oil burning produces ashes depends on its chemical composition and, above all, on the presence of contained additives. The latter are fundamental to improve the overall performances in terms of friction reduction (thus improving engine overall efficiency) and anti-wear characteristics [1-2, 4-6]. Also, they improve resistance to acid or corrosive attacks derived from combustion (especially from sulphuric and nitric acid) and reduce the tendency to foam and deposits formation (through dispersants and detergents) [2, 5-7]. However, most of these useful additives contain metals, such as Zinc (Zn), Calcium (Ca), Magnesium (Mg), Molybdenum (Mo), and other compounds, based on Phosphorus (P) and Sulphur (S), which, in case of partial combustion of oil droplets or in presence of heavy vapours inside the engine, can reach the catalytic surface and deposit on it, occluding most of its active sites, hence dramatically reducing its efficiency [1-3, 8].

2. Paper Objective

The main purpose of the present work was to determine the effects of oil consumption on an innovative exhaust after-treatment system, developed at STEMS Institute of the Italian National Research Council, after a long running period. The prototype is composed of two different stages, as represented in the scheme shown in the following Fig.1.

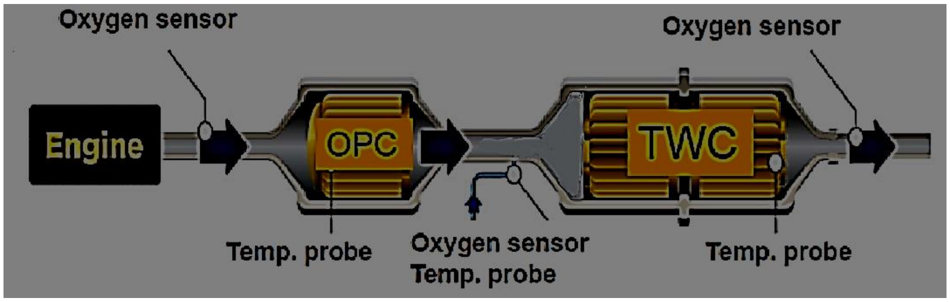

Fig. 1 Scheme of the innovative two-stage after-treatment system

The first stage is characterized by the presence of a porous SiC structure with 200 cpsi (Cell Per Square Inch) fully impregnated with Platinum (Pt) at a relative density of 25g/ft3. This element, denominated OPC (Oxidative Pre-Catalyst), has the peculiarity of having a structure which is very similar to the one proper of particulate filters usually adopted in Diesel engines. Instead, the second element is a TWC characterized by a platinum/rhodium impregnation with a 5:1 ratio and a relative density of 25 g/ft3. The first stage performs an exhaust gas pre-treatment aimed at oxidizing some pollutants (carbon monoxide (CO), unburned hydrocarbons (HC) and oil vapours), thus almost consuming all the O_2 inside the OPC while leaving most of the NOx untreated. Moreover, it enables the entrapment of a significant part of the exhaust gases inside the OPC. This is because of the SiC porous structure, which increases the mean path of the gaseous molecules, hence their mean permanence time, inside the volume of the element. In this way, two important results are achieved: the first is the complete oxidation of the organic species, such as those deriving from quenching and misfiring phenomena or from the irregularity of combustion. The second result is the mixing of exhaust gases trapped inside the pores of the element with others coming from the following cycles, with these latter characterized by different compositions and oxygen content due to the feeding control system functioning when following stoichiometry. Therefore, the porous SiC structure of the OPC performs like a physical oxygen storage, giving rise to the so called “sponge effect” and enabling a complete post-combustion of almost all the species which could not, otherwise, completely interact inside the engine. Moreover, it performs an appropriate smoothing of pressure pulses coming from the engine, considerably improving the fluid-dynamic interaction between the gas and the reactive surfaces of the following TWC. In the second stage, instead, the gas stream finds optimal conditions for its treatment. In fact, beside a relative oxygen absence, the gas is characterized by the above mentioned low compositional fluctuation and by the possibility to fix a specific feeding setting which can lead to a balanced ratio among the amounts of reducing substances (like HC and CO) and the oxidizing ones (like NOx). It should also be emphasized that the gas stream meets the oxygen sensor of the feeding control system after the treatment operated by the OPC. This implies that the sensor is no longer subjected to the typical perturbation of exhaust gases directly coming from engines, therefore, that all the instability phenomena, which could take place in the electronic feeding control system, could be avoided. Also, the oxygen sensor so positioned is able to detect stoichiometry in a more accurate way, since it also includes the oil combustion without being interested by fouling phenomena caused by deposition of post-combustion lubricant and ashes, mostly captured by the OPC [9]. In the following Fig. 2, the innovative after-treatment system is shown, with the OPC and TWC indicated with a red and a blue arrow, respectively, and with the oxygen sensor placed between the two elements.

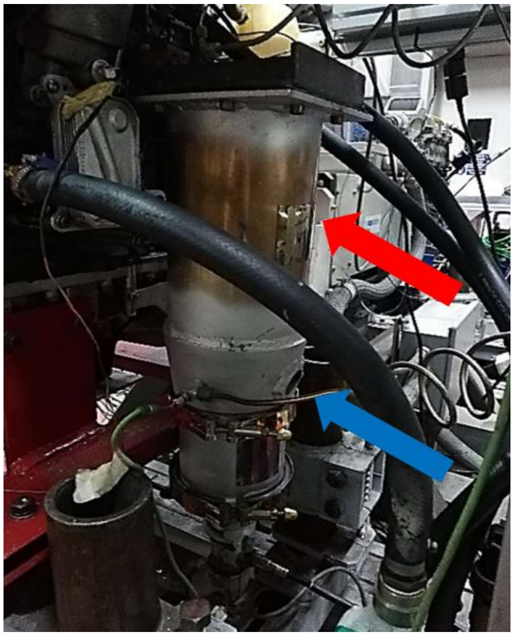

Fig.2 The innovative two-stage after-treatment system

The system has been applied to an engine fed with natural gas for small cogenerative applications, showing remarkable performances and clearly improving those obtained by means of a single-stage system. From this point of view, several tests have been conducted at STEMS laboratories in order to compare the two-stage system with a single-stage after-treatment. In particular, the innovative system has been compared with a heavy-duty TWC (HD-TWC) impregnated with a rather high concentration of noble metals (50 g/ft^3 of Pt/Rh, 5:1). The prototype has shown better performances than the HD-TWC regarding all the polluting species; in particular, towards the methane HC species, which resulted to be more difficult to oxidize, due to their much higher stability. The different performances of the two systems are reported in the following Tab.1. Each value is the mean of different three measures recorded by an API5000s based on an Emerson analyser in a temporal range of 5s. Its relative error is below 0.5%.

Tab. 1 Comparison between HD-TWC and OPC+TWC for overall emissions

	HC [ppm]	CO [ppm]	NOx [ppm]	O_2 [ppm]	Temp. [C]
Untreated	1490	5600	2580	5050	622
After HD-TWC	85	90	85	320	688
After OPC + TWC	55	30	40	85	674

As well known, however, the performance of an after-treatment system can be significantly reduced by the incoming of two different typologies of deactivating phenomena, i.e. the one based on thermal degradation and the other one based on fouling and/or poisoning of the reactive sites. In this case study, as the registered operating temperatures resulted not particularly high (even at stoichiometric regime) and far from those generally acknowledged as critical due to thermal deactivation phenomena [2- 3], the attention has been focused only on poisoning and fouling phenomena caused by the deposition of the soot produced by lubricant vapours and droplets combustion. The interest towards this potential issue is mandatory, because of the porous conformation of the OPC and of its trapping ability for particles, which could easily give rise to fouling phenomena. In fact, the latter can take place more easily in OPC than in a TWC catalyst, which is characterized only by open flow channels.

3. Experimental

In order to understand the effect of engine lubricant consumption over the catalyst, an accelerated aging test has been performed to recreate the same soot deposition condition of a long running period (almost 30.000 hours). To get to this purpose, some aging methodologies, which have been adopted in the past to introduce a certain oil amount into the engine system (and consequently to the catalyst), have been investigated [1, 3, 5]. At first, among these, those involving the direct mixing of the lubricant with the fuel have been excluded, since most of these applicative cases (cogeneration) adopt gaseous fuels. Instead, another methodology was chosen, which involves the introduction of the lubricant directly into the intake runners by means of four distinct specific pulsed electric pumps, in order to assure the same amount of oil for each cylinder. This solution, which represents the first part of the Design Of Experiment (DOE), has indicated how to introduce the lubricant into the system to simulate the effect of all oil sources in case of aged engines. These oil inputs normally derive from blow-by stream, from intake valve guides (leakages) and from worn rings, mostly sustained by pressure differences among the inner working volumes during engine running [1]. After that, the second part of the DOE was conceived in terms of defining the overall amount of lubricant which could simulate the above-mentioned running period. To achieve this result, it was determined the Specific Lubricant Consumption (SLC) for an engine which was not brand-new, but with already 2000 hours of life. As result, a SLC = 0,22 g/kWh has been recorded, the latter perfectly comparable to the one obtained for other same class engines [10] with similar wear phenomena. Thanks to this value, it was then possible to define an accelerated rate of oil consumption, which has been fixed in a value ten times higher than SLC. This amount was obtained adding further nine parts of sprayed oil in the intake ducts, dramatically augmenting engine oil consumption and making the catalyst system subject to an amount of ashes ten times higher. Furthermore, in order to stress the system and to increase even more the content of deposited ashes, it has been chosen a specific lubricant, adopted for automotive applications, which resulted to be characterized by a high additive content, corresponding to a TBN=14 (Total Basic Number), and a consequent high ash content (about 1% in weight as declared by the Producer). The percentage resulted to be five times higher than the typical value for lubricants adopted for cogenerative applications (i.e. 0,2 % in weight). This value resulted acceptable because of the adoption of natural gas as fuel (almost sulphur free), which implies a lower additive requirement (in terms of antioxidants content) and a consequently lower total basic number (TBN=5). Therefore, the adopted DOE involves a multiplication factor equal to 5 (related to the ash content of the chosen oil) and another multiplication factor of 10 (related to the increase of oil amount introduced in the system) giving an overall Ashes Introduction Factor inside the system (A.I.F.) equal to 50 times the S.L.C. This approach represented an outstanding acceleration factor for ash deposition phenomena inside the after-treatment system, so that, in order to get an equivalent running time of 30.000 hours, a total test duration of 600 hours was necessary. This would correspond to an operating period of about 6 years in case of a mean running time of 5000 hours/year (typical for small cogenerative applications). These endurance tests have been performed over a period of 4 months, with a 8 hrs daily run (from cold start) repeated 75 times. As regards the overall performance of the after-treatment system, the emission values recorded during the endurance test at the three reference positions (i.e. after the engine, after the OPC and after TWC) regarded HC, CO, NOx, O_2. In the same positions, gas temperature and local backpressure have been also recorded in order to detect any unusual value which could be related to the OPC fouling. In order to make a direct comparison of the innovative system with a conventional solution, another endurance test has been also performed on the conventional HD-TWC cited above.

4.Results

The results obtained after the whole experiment showed only a slight decrease in the overall efficiency of the innovative system, whose behaviour proved to be far away from the dramatic loss of effectiveness that normally characterizes a single-stage TWC [2], as also confirmed after the test conducted on the HD-TWC which will be later presented. As regards the prototype, in the following figures are reported, respectively, the gross gaseous emissions produced by the engine (Fig. 3), the emissions after the first treatment performed by the OPC (Fig. 4) and the emissions after TWC (Fig. 5) are reported. Each value is the result of the average of three measures recorded in a temporal range of 5s with an API5000s based on an Emerson analyser. Its relative error is below 0.5%.

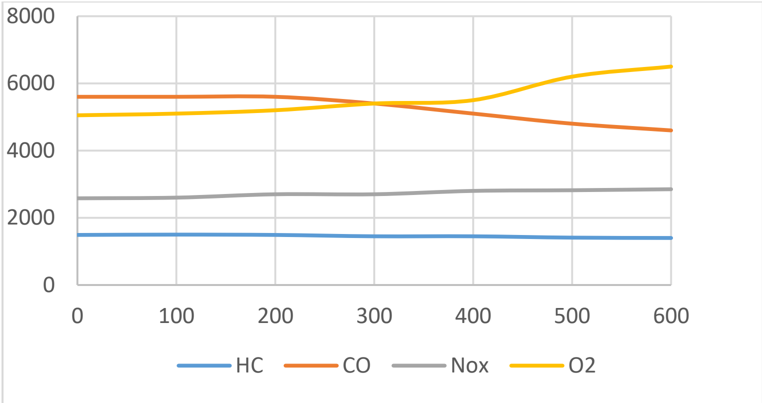

Fig. 3 Gross gaseous emissions from the I.C.E.

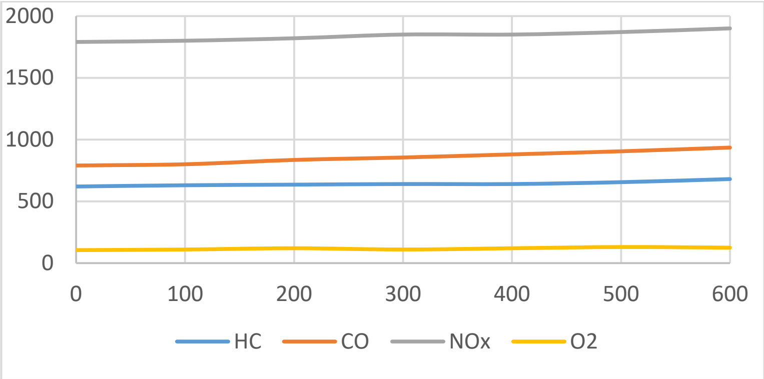

Fig. 4 Overall emissions after OPC

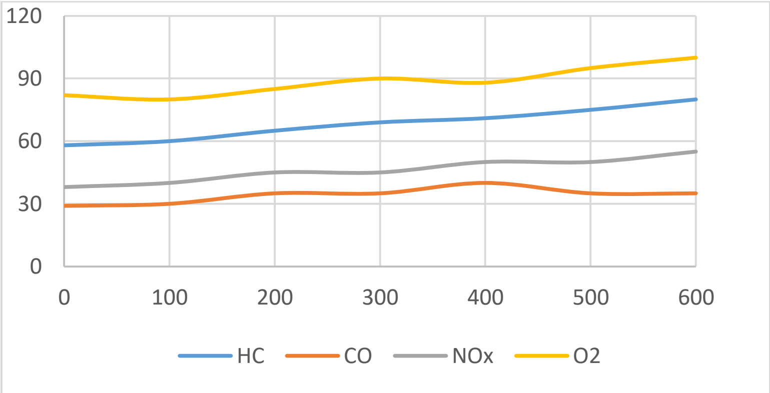

Fig. 5 Overall emissions after TWC

Instead, in the following Fig.6 and Fig.7 are, respectively, reported the exhaust line backpressure and temperature recorded in the same three different points above mentioned, i.e. after the I.C.E. after the OPC and after the TWC. Each value is the result of the average of three measures recorded in a temporal range of 5s with an API5000s based on an Emerson analyser. Its relative error is below 0.5%.

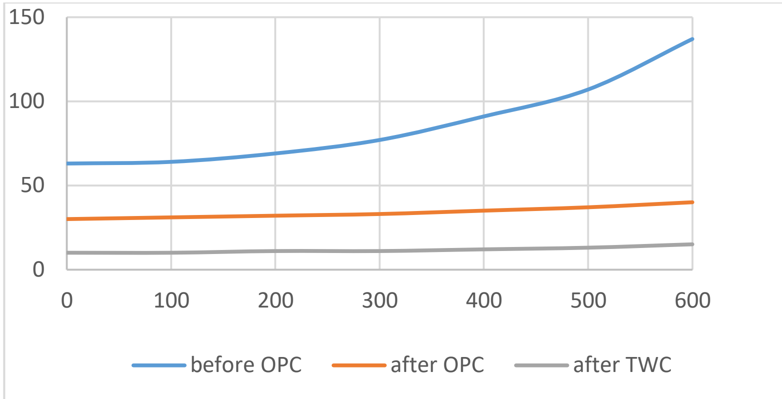

Fig. 6 Exhaust line backpressure

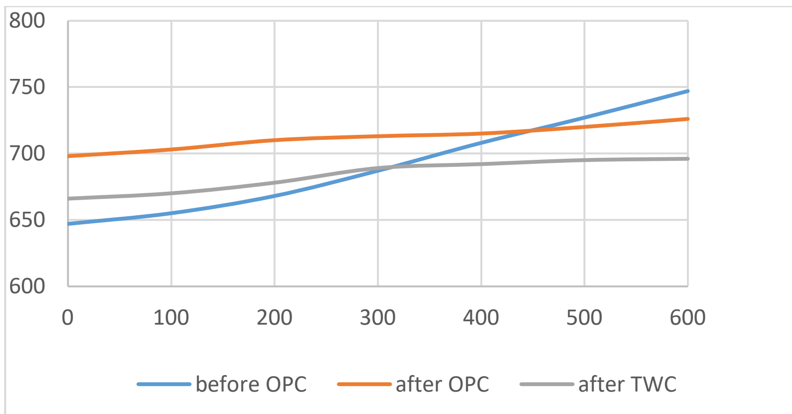

Fig. 7 Exhaust line temperatures

As it can be seen in the above-mentioned figures, the ashes captured in the OPC determine a progressive increase in backpressure and temperature values in the first part of the exhaust line between the engine and the OPC. Furthermore, after both OPC and TWC stages, an increase in HC concentration is detected, this probably due to the OPC lower oxidizing capacity, which was caused by a loss of active surface after the ash deposition process. However, CO and O_2 abatement remains substantially unchanged, as feeding control system can restore the right stoichiometry, while HC increases because of the higher oxidative reactivity of CO in respect to HC; this last aspect also involves a slight increase of NOx production inside the I.C.E., due to a leaner mixture. Moreover, it must be underlined that, even in these conditions, the TWC almost keeps its full efficiency, since it is fed only with gases in the relatively absence of O_2. Also, there are almost no heavy hydrocarbons inside, coming from partial oil burning, which can unbalance the correct ratio between the reducing substances (HC and CO) and the oxidizing ones (NOx) and almost no ashes, which can reduce the overall efficiency in terms of conversion ratios and light-off temperature [1]. These results confirmed what has been clearly demonstrated in a previous work [9] and underlined the fact that even a significant oil presence cannot reduce the overall efficiency, since it doesn't greatly affect the fundamental working principles of a TWC, thanks to the exhaust gases pre-treatment system. The TWC catalyst, on the other hand, remained almost clean after the whole experiment, also maintaining considerably lower the working temperatures (less than 650°C) compared to those of a single-stage TWC and making the reactor more durable in respect to the thermal deactivation process [1].

As regards engine performances at the end of endurance test, it has been recorded a power decrease of about 5% along with a reduction of overall efficiency of about 1,2%, due to the higher backpressure which increased pumping losses. In the following Fig. 8 and Fig. 9, the intake section of OPC before and experiment are respectively reported. It can be easily seen that a change of colour and a significant reduction of square section of intake ducts took place due to oil burning and ash deposition.

Fig. 8 The OPC before the endurance aging test

Fig. 9 The OPC after the endurance aging test

In order to calculate the effective length of the fouled zone, some rectangular probes of decreasing dimensions were adopted to measure the clean volumes. For the intake side, a significant decrease of mean cross section (about 30%) was detected, while, for exit ducts, the reduction of cross-section was quite limited (about 10%), confirming that most of the ashes remained inside the intake ducts. As regards the ash distribution, some of the previously mentioned ducts were opened by removing the closed end, this allowing to insert the probes from the back side. As result, no free length of intake ducts was detected, while it was recorded a duct section reduction of about 10% along the 65% of the original value, this confirming that ashes deposition mostly affected the first part of the OPC. It must be underlined, then, that the same fouled element could be easily cleaned by means of a treatment with oxalic acid, after which the element could easily regain almost the original cleanliness and efficiency [8, 11].
On the contrary, the TWC alone dramatically suffered the massive presence of lubricants in exhaust. In fact, as reported in the following Tab.2, HD-TWC overall emissions resulted much higher than those recorded for innovative systems, resulting unacceptable for the current regulation regarding gaseous emissions for cogenerative plants. Moreover, an increase of temperature was detected, probably derived from the afterburning of heavy hydrocarbons inside the system. For this reason, the test was interrupted after a running period of just 100 hrs. These results confirm that in case of oil contamination the TWC loses all the mandatory conditions for satisfactory behaviour because of the contemporary presence of oxygen, unburned oil and ashes, which completely upset the essential chemical balance.

Each value shown in the following Tab.2 is the result of the average of three measures recorded in a temporal range of 5s with an API5000s based on an Emerson Analyser. Its relative error is below 0.5%.

Tab. 2 Overall emissions after HD-TWC

	HC [ppm]	CO [ppm]	NOx [ppm]	O_2 [ppm]	Temp. [C]
Untreated	1490	5600	2580	5050	622
HD-TWC (new)	85	90	85	320	688
HD-TWC (100 hrs)	1645	2130	740	885	724

4.Conclusions

The innovative after-treatment system has shown very interesting performances in terms of constancy of behaviour, even in case of extended running periods. The above seen remarkable performances derive directly from the robust concept adopted for this system, which determines a strong oxidation process for exhaust gases through an oxidative pre-catalyst (OPC). This latter aims to stabilize the exhaust composition and to almost eliminate substances (like O_2), which can limit some reactions (i.e., the NOx reduction) or poison the catalyst, while keeping a perfect balanced ratio between reductive and oxidative substances. This concept results very well suited also for oil contaminated exhaust gas, because the OPC acts like an efficient reactor which can avoid the lubricant burning inside the TWC, keeping the latter element far from unbalanced chemical reactions and well protected from the deposition of ashes derived from oil oxidation. In conclusion, this unconventional after-treatment system could assure very low emissions quite along the entire lifetime of the system, being the same not much affected by fouling phenomena, thus offering to most cogeneration systems the chance to be comparable in performance with the state of art emissions of centralized big power plants.

5. References

[1] S.V. Kumar, “Influence of Phosphorous Poisoning on TWC Catalysts”. SAE Technical Paper, 2003-01-3735 2003. https://doi.org/10.4271/2003-01-3735.

[2] J, Franz, J. Schmidt, C. Schoen, M. Harperscheid, S. Eckhoff, M. Roesch, J. Leyrer, “Deactivation of TWC as a function of oil ash accumulation-a parameter study”. SAE Technical Paper, 2005-01-1097 2005. https://doi.org/10.4271/2005-01-1097

[3] M.C. Galassi and G. Martini, “Durability demonstration procedures of emission control devices for Euro 6 vehicles” *EUR 26435. Luxembourg (Luxembourg): Publications Office of the European Union, 2014, JRC87070*. Available: https://publications.jrc.ec.europa.eu/repository/handle/JRC87070

[4] T.J. Toops, M.J. Lance, J. Qu, M.B. Viola, S.A. L. Donovan N., E.W. Hagaman, X. Chao Mon “Impact of Lubricant Additives on the Physicochemical Properties and Activity of Three-Way Catalysts”, *Catalysts*, 6(4), 2016, p.54 https://doi.org/10.3390/catal6040054.

[5] K. Stork, “*FY 2013. Progress Report for Fuel & Lubricant Technologies”*. Washington D.C., EERE Publication and Product Library, 2014.

[6] S. Korcek, J. Sorab, M.D. Johnson, R.K. Jensen, “Automotive lubricants for the next millennium”, *Industrial lubrication and Tribology*, 52 (5), 2000, pp. 209 – 220. https://doi.org/10.1108/00368790010373175

[7] N.S. Ahmed, H.S. Abdel-Hameed, A.F. El-Kafrawy, “Preparation, characterization, and evaluation of some ashless detergent/dispersant additives for lubricating engine oil.” *Applied Petrochemical Research,* 6(1), 2016, 49-58

[8] V. Kröger, “Poisoning Of Automotive Exhaust Gas Catalyst Components, The role of phosphorus in the poisoning phenomena” Ph.D. dissertation, Dept. of Process and Environmental Engineering, Oulu Univ., Oulu, Finland.

[9] F.M. Grimaldi and P. Capaldi, “An innovative exhaust gas after-treatment for a two stroke microcogeneration unit” in *Proceedings of the 42th Meeting of the Italian Section of the Combustion Institute*, Ravenna, RA, Italy, 2019, session V7, pp. 180-185.

[10] Piston and Engine Testing, Mahle GmbH, Springer Fachmedien Wiesbaden, Ed. Stuttgart, 2012, pp. 115-280.

[11] S.T. Darr, R.A. Choksi, C.P. Hubbard, M.D. Johnson, R.W. McCabe, “Effects of oil-derived contaminants on emissions form TWC-equipped vehicles.” SAE Technical Paper 2000-01-1881, 2000, https://doi.org/10.4271/2000-01-1881.