NOVEL CATALYTIC CONVERTER OXIDE FOR SI ENGINES

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Abstract

Subject of the paper are converters of lean mixtures for SI engines with a good efficiency of NOx reduction. Investigation of new effective catalytic materials having good sorptive properties of nitrogen oxides and simultaneously resistant on the thermal destruction and chemical destruction are main aim of the paper. The operating idea of such converters and conditions of their work are also presented. Main objective of the paper is performance of the new reactor of the Pt/Rh-MgO/CeO2/Al2O3 formula. The magnesium oxide MgO is here an absorber of nitrous oxides and has an essential feature, it is resistant on sintering. Such reactor can be the alternative for generally applied converters containing the barium oxide. Experimental results of catalytic converter containing various quantities of magnesium oxide for SI engines with lean mixtures are presented in the paper. Researches involved both laboratory and engine tests. The laboratory researches concern the topography active surface of the reactor with the scanning electron microscopy) method. Size of platinum and rhodium crystallites obtained from the Scherrer dependence analyzing the diffractive spectrum of the X-radiation (XRD) was about 5 nm. Moreover method covering of reactor's active layers on the metal- monolith is presented. Engine researches comprised CO, THC, and NOx conversion for two engines in conditions of lean (A/F=20.0), reach (A/F=14.0), and stoichiometric (A/F=14.7) mixtures. CO, THC, and NOx conversion were stated in the dependence of temperature catalytic process in conditions of the various mixtures:

Keywords: *combustion engines, ecology, exhaust emission, lean mixtures, catalytic converters*

1. Introduction

SI engines generally run on stoichiometric air/fuel mixtures with A/F = 14.7 and λ = 1.0) in order to be compatible with the functional requirements of the three-way catalysts. Due to the combustion reactions, CO_2 emissions are highest with stoichiometric engine settings. For minimum fuel consumption, the optimum A/F ratios are in the lean-mixture range with λ = 1.2 to 1.5 (A/F = 17 - 22). Besides complying with future exhaust emission legislation, combustion engines will make a significant contribution towards reducing CO2 emissions. Current SI and Diesel engine developments reveal a trend towards hybrid combustion systems, which are becoming increasingly similar. The engine concepts presenting the greatest potential for the reduction of fuel consumption and CO_2 emissions are the following ones:

- lean-burn engines operated on a homogenous A/F mixture,
- lean-burn engines with direct fuel injection,
- stratified-charge engines,
- engines with variable valve timings.

On the other hand, most of research works with reference to piston engines with the direct fuel injection concentrate on two basic systems. One system is a homogeneous system and refers to high engine loads both from the point of view of torque and rotational engine speed. The second system refers to small loads and rotational engine speeds which usually do not exceed 50% of the maximum allowable loads and the rotational engine speed (Fig. 1). This system is a heterogeneous system. Ideas relating to two names are speculative ideas and Ideas relating to two names are speculative ideas and essential conditions occurring in an engine significant differ from homogeneous conditions and heterogeneous ones, where also homogeneous areas are visible.

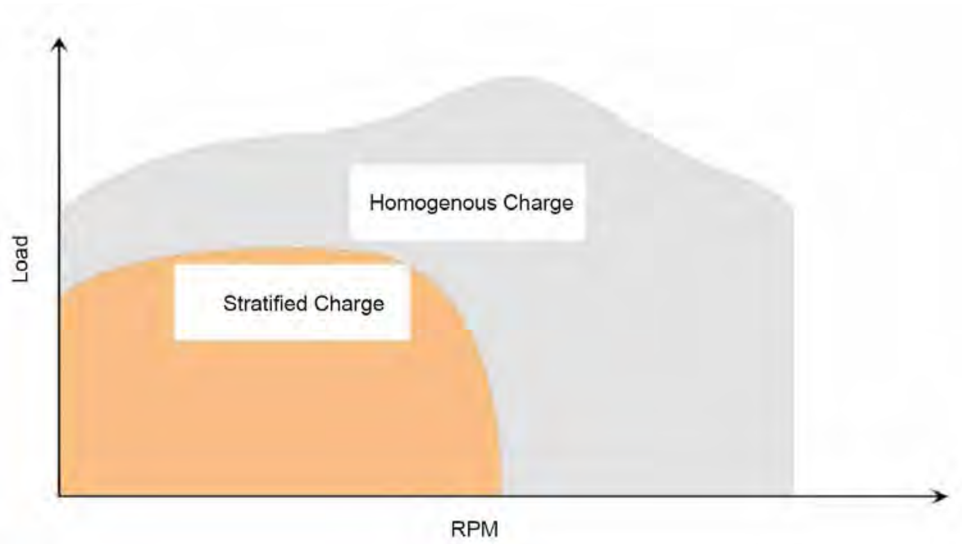

Fig. 1. Two strategies of the power supply of with the spark-ignition engines with the direct-injection: the stratified charge at small loads an d rotational s peeds and the homoge neous charge at big loads and r otational speeds of the engine

The first system, the homogeneous system, is also characterized that it can be applied both with reference to Diesel and spark-ignition engines. This system is characterized with the early fuel injection, usually during the intake stroke. So there is a lot of time for proper (homogeneous) preparation combustion mixture which should be homogeneous. However even uniform distribution of the fuel in combustion chamber does not give the full view of qualitative and quantitative preparation of the mixture. The quality of injected fuel spray has a very big meaning for obtainment of correct work parameters of the engine referring to torque, fuel consumption and emission level of exhaust gases. Preliminary researches showed that the quality of injected fuel spray having very essential importance for the obtainment of suitable parameters engine work was name only homogeneous spray, and practically her homogeneity refers to the macro scale. Such approach for the problem is a strong simplification. Such approach for the problem is a large reduction, if the accepted name of the homogeneous charge has to be applied. Uniform fuel distribution in combustion chamber differs only this system from second one where fuel can be not uniform distributed in combustion chamber and can also appear areas where there is not fuel at all.
In the second work system, the heterogeneous system, fuel is heterogeneously distributed in combustion chamber. In this system of engine work, fuel injection occurs close to end-point phase of compression stroke. So, there is a little time for combustion mixture preparation. However in the zone of the mixture ignition should be homogeneous and fuel spray should be characterized with small dimensions of fuel droplets. This refers especially for so called "the cold" ignition which at the heterogeneous mixture can not appear or miss fire will appear, what negatively affects on engine economic parameters and emission level of exhaust gases. In this second system the exchange and thermal conditions have essential influence on the correct process run of the combustion and emission level of exhaust gases.

The need to decrease fuel consumption and reduce the emission of carbon dioxide by automotive vehicles has led to development of technologies making it possible to burn lean A/F mixtures in spark-ignition engines. Such engines, e.g. FSI engines manufactured by Volkswagen, or HPI engines manufactured by PSA, burn lean layered mixtures with A/F ratio up to 50, ant their exhaust gas contains even more than 10% oxygen. General characteristics of combustible mixture composition of FSI engine having displacement $V_{ss} = 2.0\ dm^3$, is shown in Fig. 2. The catalytic reactor of such an engine should attain as high as possible conversion rates of CO, THC, and NO_X during combustion of:

- very lean layered mixture (A/F values from ~30 to ~50),
- homogenous lean mixture (A/F up to ~30),
- homogenous stoichiometric mixture (A/F=14.7).

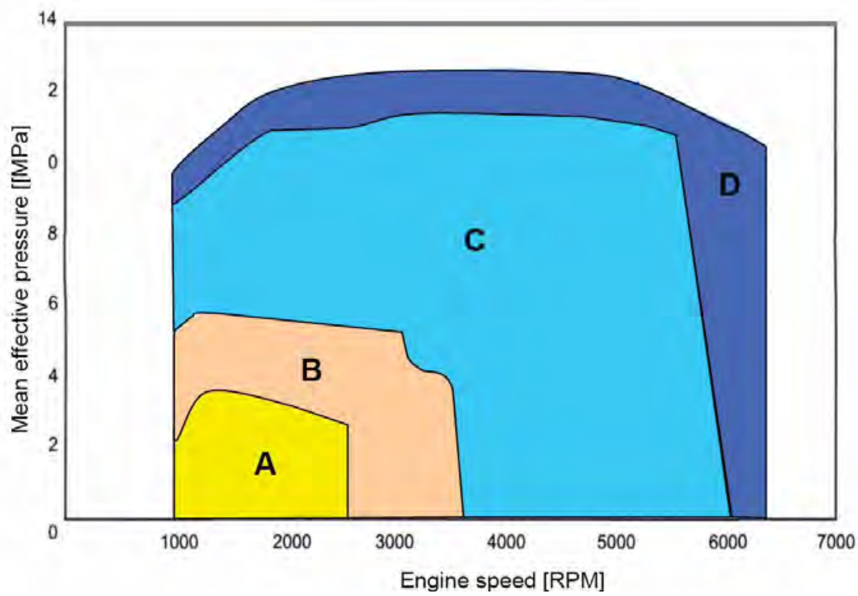

Fig. 2. General characteristics of combustible mixture composition of an engine burning of lean layered mixtures

Legend:

A - very lean layered mixture (A/F values from ~30 to ~50), with exhaust gas recirculation,
B - homogenous lean mixture (A/F up to ~30) without exhaust gas recirculation,
C - homogenous stoichiometric mixture (A/F=14.7) with exhaust gas recirculation,
D - homogenous stoichiometric mixture (A/F=14.7) without exhaust gas recirculation.

When working under combustion conditions of lean A/F mixtures, the classic three-function catalytic reactor - TWC (Three Way Catalyst) – exhibits very poor efficiency of NO_X reduction. Because of that, technologies were developed in order to design reactors making it possible to remove NO_X in presence of oxygen in exhaust gas. Such reactors are referred to as nitric oxides traps - LNT (Lean NO_X Traps), or reactors storing and reducing nitric oxides - NSR-Catalysts (NO_X Storage Reduction Catalysts). The working cycle of said reactors during combustion of very lean layered mixture can be divided into two phases:

- a long phase of storing nitric oxides (very lean layered mixture, A/F>14.7),
- a short phase of reducing nitric oxides (instantaneous pulse of reach mixture, A/F<14.7).

The mechanism restricting the emission of NO_X is as follows (see Fig. 3). During the first, i.e. storage phase, NO reacts with O_2 giving NO_2, which in turn gives thermally stable nitrates with alkalic oxides. In this way, NO_X gradually covers the storing material, and the reactor saturates with nitric oxides. During the second phase, i.e. reduction phase (instantaneous pulse of rich mixture), nitric oxides are released and non-selectively reduced by CO, THC and H_2, as this takes place in classic three-function reactor [1].

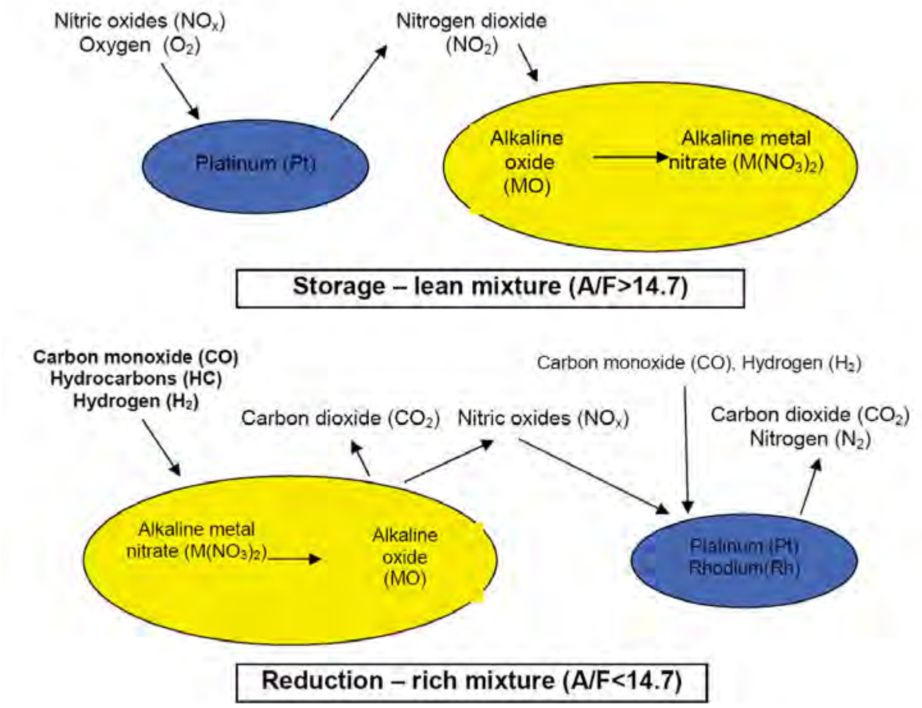

Fig. 3. Reaction diagram of storage and reduction of nitric oxides in catalytic reactor containing oxides of alkaline metals and of rare earths metals

Properties of materials adsorbing nitric oxides are currently subject of intensive scientific research work [1-5]. Researchers have tested, among many others, adsorption characteristics of oxides of metals and rare earths metals (lithium and beryllium) such as Ca, Na, K, Ba, Sr, Cs, and Mg. Properly functioning LNT catalytic reactors should efficiently remove CO, THC, and NO_X from exhaust gas, as well during combustion of stoichiometric mixtures as during permanent or periodical combustion of lean mixtures. The present paper is intended to present the characteristics of new type of LNT reactor, in which NO_X are stored using alkaline magnesium oxides.

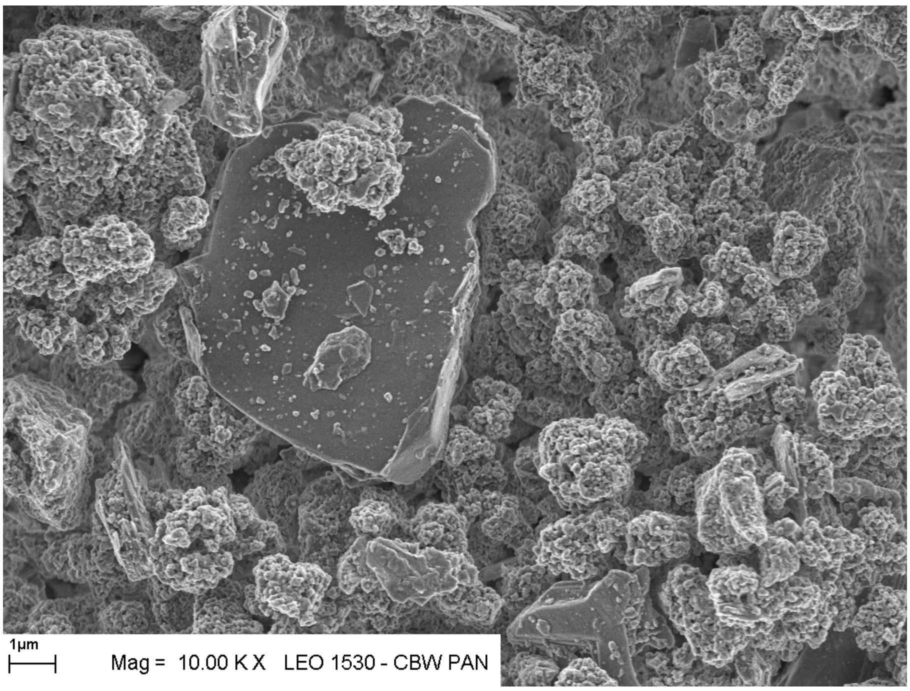

Fig. 4. Active surface of Pt/Rh-MgO/CeO2/Al2O3 reactor, magnification 10 000×, scanning electron microscope (SEM)

2. Test reactor

The model of NO_X trap reactor, designated as $Pt/Rh\text{-}MgO/CeO_2/Al_2O_3$ with NO_X storing component in form of magnesia, was built on steel foil monolith with 64 ducts per cm^2, coated with active catalytic support in form of composition of oxides, namely 30% MgO, 10% CeO_2, 60% Al_2O_3 amounting to 130 g/dm^3, and then impregnated with precious metals, namely Pt and Rh, giving 2.8 g/dm^3 and 1.1 g/dm^3 respectively. Dimensions of reactor model in form of cylinder were: Ø=36mm, length l=70 mm.

The picture of reactor active surface obtained using scanning electron microscope (SEM) is shown in Fig. 4.

XRD tests of reactor active surface were carried out using D5000 Siemens-Bruker AXS diphractometer with Cu lamp, using characteristic radiation line CuKα with wavelength λ=1.54184Å. Fig. 5 shows a fragment of diffraction spectrum, from which one can, using Scherrer's relationship, determine the size of platinum crystallites being equal to 5 nm approximately.

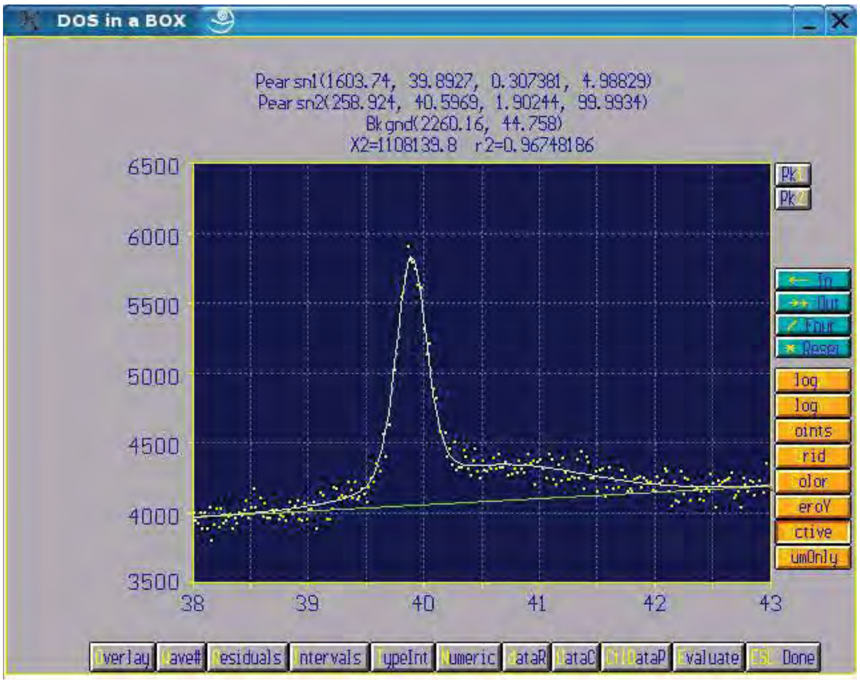

Fig. 5. Fragment of diffraction spectrum of Pt/Rh-MgO/CeO2/Al2O3 reactor surface

3. Test procedure

The model of the reactor was tested on HX 4000 Honda engine, adapted to burn homogenous lean mixtures (A/F=20), and on Rover K16 engine, burning stoichiometric mixtures. The model was placed in an electric tubular furnace, allowing for free adjustment of catalytic conversion temperatures. Relative volumetric flow rate of exhaust gas was SV= 20000 h^{-1}. Concentration of exhaust gas components were recorded before and after the model of reactor being tested, at 0.5Hz frequency. Tests were carried out using the following cycle:

- recording of exhaust gas components of Honda HX 4000 engine during 60s period of engine run supplied with rich mixture (reactor reduction - A/F=14.0), and abrupt switching to supply with lean mixture (NO_X storage - A/F=20.0) for 100s run. Such a recording was carried out for constant conversion temperatures, 160ºC, 207ºC, 269ºC, 300ºC, 357ºC, and 407ºC respectively,
- calculation of current conversion of CO, THC and NO_X during concentration recording,
- calculation of average conversion of CO, THC and NO_X in cycles simulating real working

conditions of an engine burning layered lean mixtures. Said cycles (reduction period + storage period) were as follows:
- cycle - 6s (A/F=14.0) +18s (A/F=20.0),
- cycle - 6s (A/F=14.0) +36s (A/F=20.0),
- cycle - 6s (A/F=14.0) +54s (A/F=20.0),
- cycle - 6s (A/F=14.0) +72s (A/F=20.0),
- cycle - 6s (A/F=14.0) +90s (A/F=20.0).

- calculation of conversion rate of CO, THC and NOX during final phase (reactor saturation phase) of engine run on lean mixture (A/F=20.0),
- recording of concentration and calculation of conversion rate of CO, THC and NOX as functions of conversion temperature for Rover K16 engine supplied with stoichiometric mixture A/F =14.7±0.15 oscillatory variable at f = 1.8Hz.

Block diagram of the test stand is shown in Fig. 6.

Figure 7 shows examples, recorded in constant catalytic conversion temperature t = 269ºC, conversions of CO, HC and NOX concentration during approx. 60 s engine run on rich mixture (A/F = 14.0), and, after abrupt transition, during next 100 s period of engine run on lean mixture (A/F = 20.0).

Using so acquired data, also for other catalytic conversion temperatures, mean conversions of CO, THC and NOx in cycles simulating real working conditions of an engine burning layered lean mixtures (Honda HX4000) were calculated, and said results are shown as functions of temperature in Fig. 8-10, respectively.

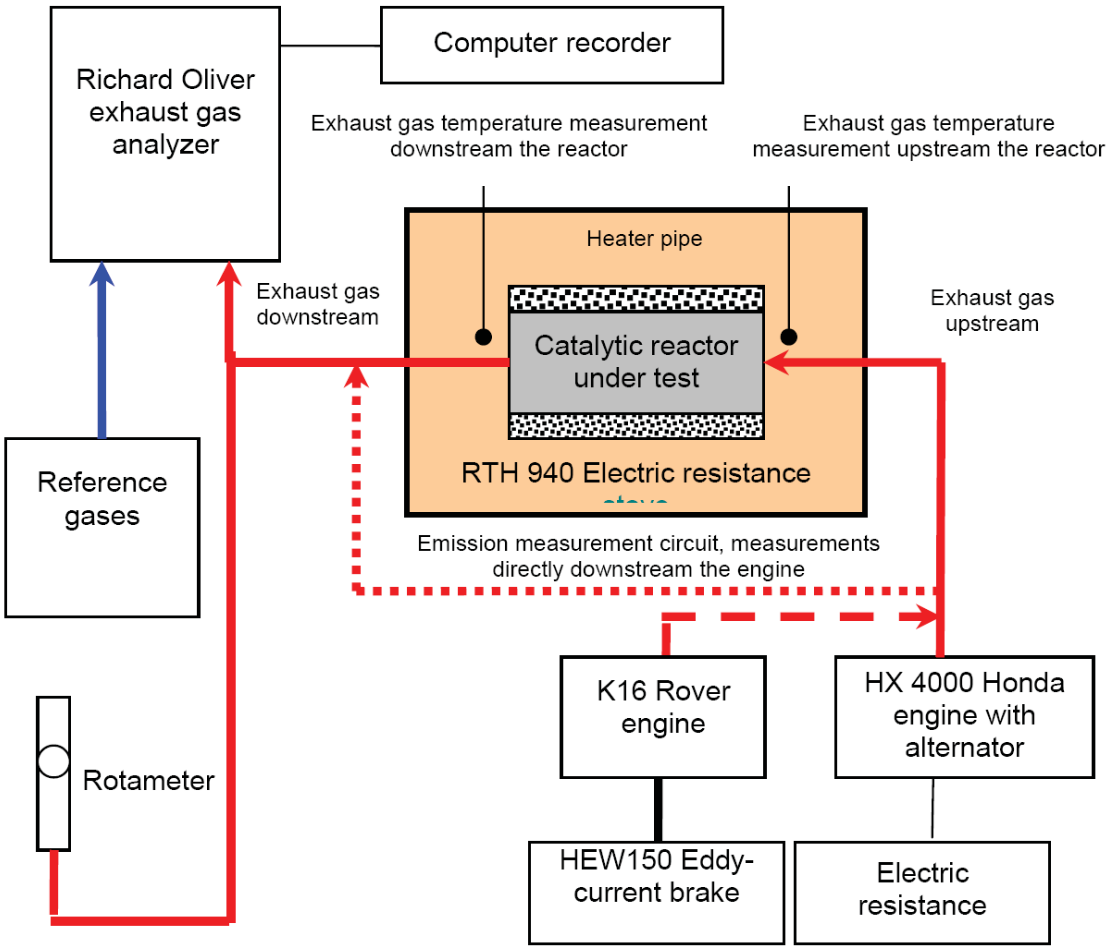

Fig. 6. Block diagram of test stand

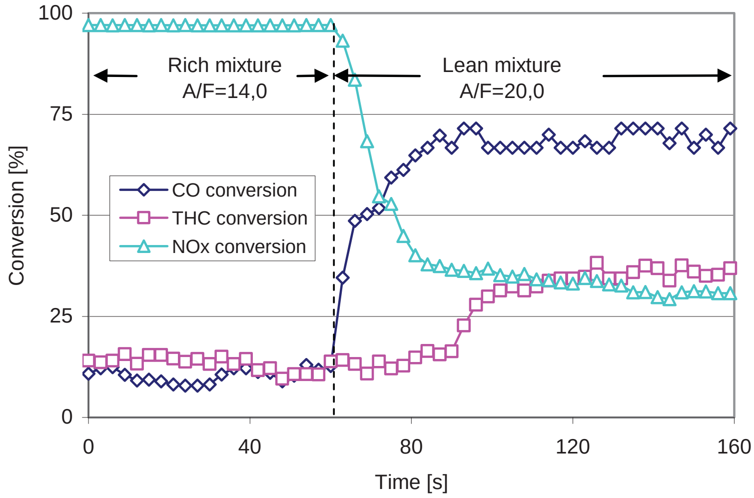

Fig. 7. Examples of calculation results of CO, THC and NOx conversion at 269°C during 60 seconds engine run on rich mixture, and 100 seconds on lean mixture

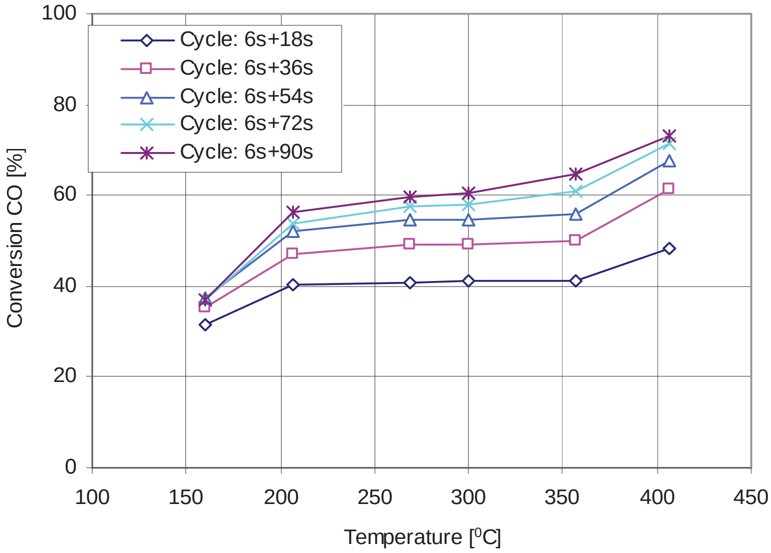

Fig. 8. Calculation results of CO conversion as function of catalytic process temperature for assumed cycles (reduction period + storage period)

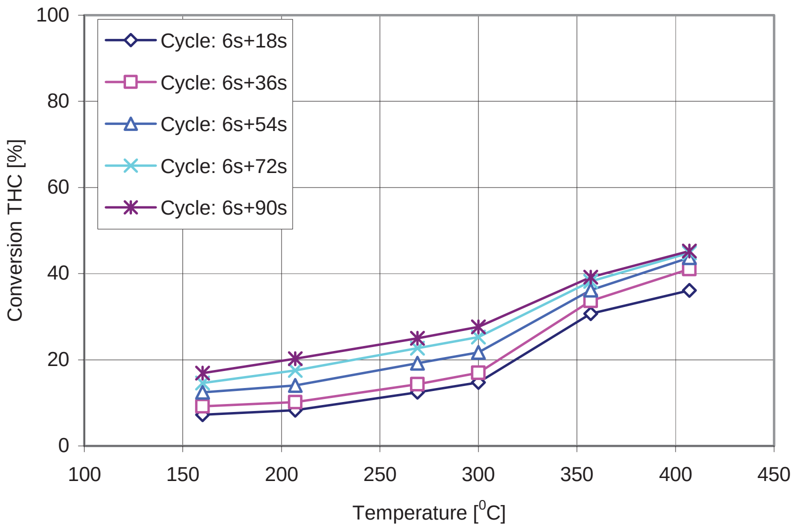

Fig. 9. Calculation results of THC conversion as function of catalytic process temperature for assumed cycles (reduction period + storage period)

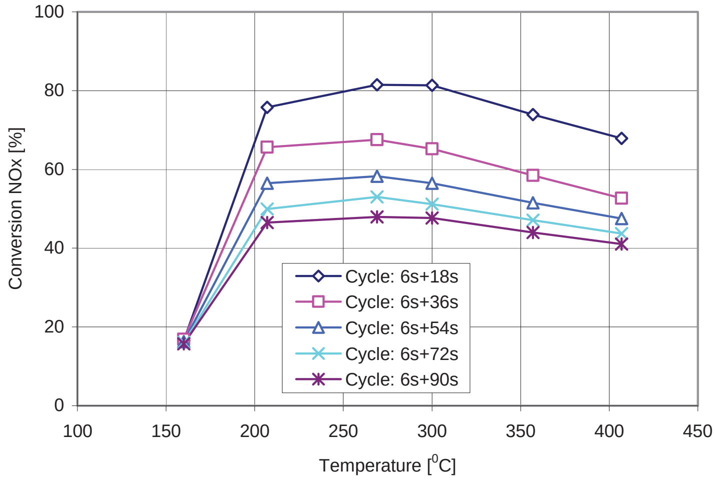

Fig. 10. Calculation results of N OX conversion as function of catalytic process temperature for assumed cycles (reduction period + storage period)

Calculations of CO, THC and NOx conversion during continuous combustion of lean mixture A/F=20.0 (Honda HX4000 engine) are shown in Fig. 11.

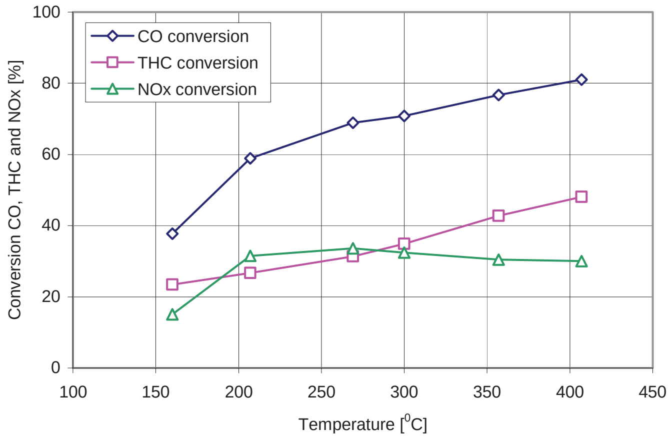

Fig. 11. CO, THC and NOx conversion during combustion of lean mixture A/F=20.0 as function of temperature

Calculation results of CO, THC and NOx conversion during combustion of stoichiometric mixture A/F=14.7 (Rover K16 engine) are shown in Fig. 12.

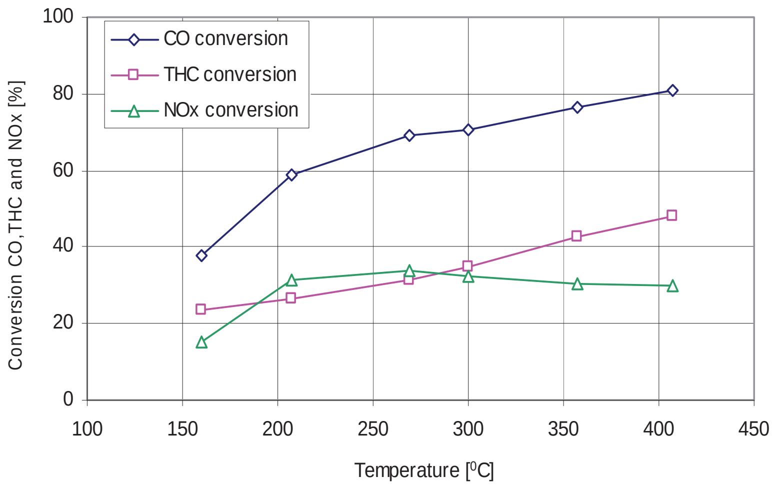

Fig. 12. CO, THC and NOx as function of catalytic process temperature during combustion of stoichiometric mixture

4. Conclusions

Lean burning can take in the knock burning. Lean burning has a high potential for improving thermal efficiency. However, the potential of lean boost burning for knock suppression is limited in the specific engine output. Therefore, significant improvement of output can not be expected only by lean mixture. In lean burning with increasing air flow, the auto-ignition reaction in end-gas is promoted by elevated temperature and pressure rather than suppressed by the dilution. As a result, the increased air flow brings the mixture closer to compression ignitable state. In lean burning with increased of air flow with constant fuel flow can not suppress knock compared with stoichiometry while it can with decreased fuel flow with constant air flow.

The elaborated model of reactor, nitric oxides trap, comprising magnesia in its formulation, oxidizes CO and THC, and reduces NO_X under periodically variable conditions of burning of lean mixtures:

- oxidizing and reducing characteristics of the reactor strongly depends on variation cycles of mixture composition, i.e. lean-to-rich and rich-to-lean cycles used,
- for shorter run periods on lean mixtures NO_X conversion decreases, with simultaneous increase of CO and THC conversion,
- maximum NO_X conversions exceeding 80% are obtained by the reactor in question during 6 s cycle (A/F=14.0) +18s (A/F=20.0) within comparatively narrow temperature range of 250-320ºC,
- storage properties of NO_X, being decisive for possible extension of its run period on lean mixtures up to and over 60s; however, for the reactor in question they are still insufficient, and a modification of catalytically active components is required.

1. The reactor elaborated assures, during continuous burning of lean mixtures, comparatively high conversion of CO reaching up to 80% at temperatures of 400ºC approximately. THC and NO_X conversions are definitely lower and are comprised between 20-50% within temperature range under test.
2. Under burning conditions of stoichiometric mixtures, said reactor obtains maximum conversion of CO, THC and NO_X of 90% at temperatures above 500ºC, and 50% conversion temperatures (light off) are within 400-450ºC.

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