

The analysis of diesel engine performance equipped with inner catalyst

The paper presents the results of the research focused on the effect of inner catalyst on diesel engine operating performance. The active factor was applied on the engine valves surface and implemented into combustion space. The method of inner catalyst preparation is shown. The methodology of the engine's test in the laboratory is proposed, too.

Platinum and rhodium were applied as active factors. The plasma-sprayed zirconium ceramic was used as catalyst support. The ceramic coating contributes also a local thermal barrier and causes increasing the temperature in zone of catalyst application what can result in catalyst effectiveness improvement.

The engine's test bed was equipped with in-cylinder pressure and temperature measurement systems. Several engine's operating parameters were tested e.g.: engine power, engine speed, fuel consumption and exhaust gases toxicity (especially PAHs and VOCs concentration).

Key words: diesel engine performance, inner catalyst, polyaromatic hydrocarbons, volatile hydrocarbons

Analiza paramentów pracy silnika o zapłonie samoczynnym wyposażonego w katalizator wewnętrzny

W pracy przedstawiono wyniki badań, których celem była ocena wpływu zastosowania katalizatora umieszczonego wewnątrz cylindra silnika o zapłonie samoczynnym na parametry pracy tego silnika. Zaprezentowano metodę preparatyki katalizatora jak również metodę oceny skuteczności zaproponowanego rozwiązania na stanowisku hamownianym.

Jako czynnik aktywny katalitycznie podczas realizacji badań wykorzystano platynę oraz rod. Warstwę nośną katalizatora stanowiła ceramika cyrkonowa naniesiona metodą natryskiwaną plazmowego na wybrane elementy silnika (zawory silnikowe). Warstwa ceramiczna stanowiła nie tylko nośnik katalizatora pozwalający rozwinąć jego powierzchnię ale również lokalną barierę termiczną.

Stanowisko do badań silnikowych (hamownia) wyposażona była w układ pomiaru ciśnień i temperatur wewnątrz cylindra. Monitorowano następujące parametry: moc silnika, zużycie paliwa jak również toksyczność spalin (w szczególności emisję szczególnie toksycznych wielopierścieniowych węglowodorów aromatycznych oraz lotnych związków organicznych).

Słowa kluczowe: silnik o zapłonie samoczynnym, katalizator wewnętrzny, wielopierścieniowe węglowodory aromatyczne, lotne związki organiczne

1. Introduction

The use of an oxidative catalyst applied to the walls of the combustion chamber as a method for reducing diesel exhaust emission has recently been proposed by several researchers. The reported results of the in-cylinder catalysis impact on engine performance and the reduction of gaseous pollutant are discussible. According to some authors' opinions inner catalyst is advantageous and prospective solution [1, 3, 4], for some authors the impact of the solution is insignificant, few investigations prove that active factor in combustion space cause disadvantageous phenomena as i.e. "quenching effect" intensification [2].

Taking into consideration recent researches concerning diesel exhaust impact on human health

[4,5] very important indicator of vehicular emission became specific organic compounds like polyaromatic and volatile hydrocarbons because of their mutagenic and carcinogenic properties [4, 5]. The stage of the engine combustion process which is suspected as a cause of those compounds emission is ignition delay period [4].

It is suspected that the active agent i.e. a precious metal affects the fuel combustion process by catalyzing the fuel-air combustion reaction, especially prior-combustion reactions what is correlated with shortening of combustion delay period [6, 7]. One of the authors suggestion is that the active agent put into combustion space causes start of complex chain reactions and the phenomena is related with shortening of time of chemical auto-ignition delay.

Based on references [4, 6, 7] it is possible to conclude that modification of combustion space by catalytic active agent implementation may, with significant probability, cause shortening of fuel-air mixture auto-ignition delay time in the internal combustion engine what may ensure lower toxic hydrocarbons emission [4].

The authors of this paper during the researches tried to evaluate the in-cylinder oxidation catalyst impact on contemporary diesel engine performance including the most toxic substances emission like polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs).

2. Inner catalyst preparation

Thick plasma sprayed thermal barrier coatings (TBC) is used as a catalyst support. zirconium, yttrium-stabilized ceramic, because of its special properties, is well known, suitable for thermal and hot corrosion protection material which is often use for diesel engines applications. In addition, they represent potential solutions to increase the engine efficiency, in terms of higher combustion temperature and reduced cooling air flow, and to reduce the fuel consumption.

As a catalyst carrying zirconium ceramic layer was used. A scheme of the inert catalyst is shown in the figure 1.

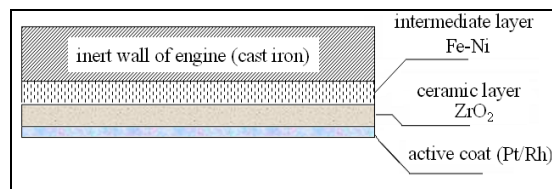


Fig 1. Scheme of the inner catalyst.

3. Experiment

The researches was carried out in the Division of Motor Vehicles and Internal Combustion Engines laboratory at the Wroclaw University of Technology. The SB3.1. diesel engine was employed as the research engine. The lay-out of the engine test bed is presented on figure 2.

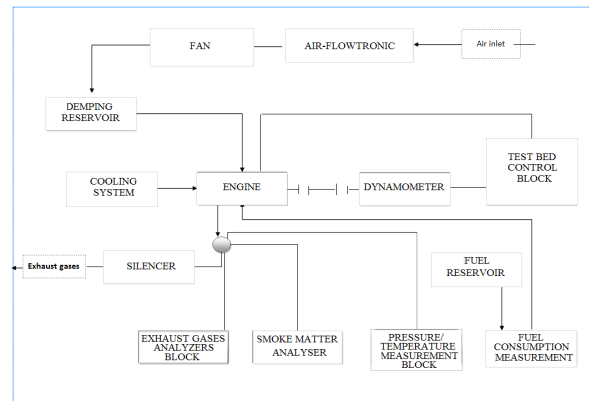


Fig. 2. The lay-out of the research test bed

The test bed was equipped with in-cylinder pressure and temperature measurement systems. The system for data register and acquisition based on measurement channel with piezoelectric sensor, impulses amplifier, oscilloscope and software for signal processing software. Each pressure diagram has been averaging of 600 to 800 engine's cycles.

The engine modification was platinum-rhodium application on the engine valves surface. Plasma-sprayed, zirconium ceramic coating was used as a catalyst support. The ceramic coating acted simultaneously as a thermal barrier caused a local temperature increase.

The direct signals was put into several mathematical transformations connected with signal filtering and measurement channel calibration to eliminate potential disturbances. In the signal filtering process the signal aggregating method and average values weighting method were used.

The methods error was estimated as 0,01 MPa for range 0 to 5 MPa and 0,03 MPa for range 0 to 10 MPa. The difference in error level is an effect of signal transformations on values of pressure for various signal amplifications in the amplifier and the oscilloscope.

The tests were done for chosen engine speeds: 1200 rpm, 1400 rpm and 1600 rpm and crank angle degrees of fuel injection advance: 20 deg, 23 deg and 27 deg in crank angle. Two states of engine work were studied and compared: without and with inner catalyst. Average real operational engine load, 47,7 Nm, was chosen for pressure diagram analysis for each engine speed.

4. Analytic method

Volatile Organic Compounds

VOC's samples were up-taken by tubes with active coal (ex. prepared). Formaldehyde was up-taken by special absorption bulb with distilled water. The analysis was done according to polish standard: PN – EN ISO 16017-1: 2006. The laboratory analysis contains two analytic methods: colorimetry (formaldehyde marking according to directive PN-

71/C-04539) and chromatography. Gas chromatograph Varian 450 GC with FID detector was used for quantity and quality analysis. The chromatography conditions were: column temperature (110°C), dozers (150 °C) and detectors (250 °C).

Polycyclic Aromatic Hydrocarbons

PAHs analytic method based on few important stages: uptake stage, research material recovery, sample purification and enrichment, chromatography analysis. Because of unstable parameters of engine work (pressure and temperature jumps) PAHs samples was up taken by tubes with active coal, type SKC-lot 120, (gas phase) and by Staplex TF AGF 810 filters (PAHs adsorbed on particle matter). According to new analytic recommendations Solid Phase Extraction was used for sample purification. Gas chromatograph Varian 450 GC with FID detector was used for quantity and quality analysis. The calibration was made by attested mixture of 16 model samples (according to EPA, USA). The temperature was programmed in the range 60 – 280 °C with 15 deg/min increase.

Engine Parameters for PAHs and VOCs Sampling

The parameters of engine work for PAHs and VOCs sampling are presented in table 1.

Tab 1. Parameters of engine work for hydrocarbons sampling

Engine speed, rpm]	Engine load, Nm	VOCs	PAHs
1200	5	+	+
	10	+	
	20	+	
	30	+	+

5. Results and discussion

The maximum in-cylinder pressures ignition of the combustion process, crank angle before TDC, and the ratio of dp to da , MPa/deg for both engine states on each analyzed engine speed are presented in table 2.

Tab 2. Maximum in-cylinder pressure, ignition of the combustion process, crank angle before TDC, and the ratio of dp to da , MPa/deg for various engine speeds and both states of engine work

Crank angle fuel injection advance, deg	Maximum in-cylinder pressure, MPa					
	1200 rpm		1400 rpm		1600 rpm	
	Without catalyst	With catalyst	Without catalyst	With catalyst	Without catalyst	With catalyst
- 20	4,59	4,97	4,48	4,76	4,27	4,59
- 23	5,06	5,03	4,85	4,91	4,73	4,65
- 27	5,03	5,57	4,76	5,30	5,30	5,30

Start of the combustion process, crank angle fuel injection advance, deg						
- 20	- 1,10	- 4,70	- 3,40	- 4,20	- 2,30	- 5,60
- 23	- 3,24	- 4,96	- 4,19	- 4,58	- 2,86	- 3,82
- 27	- 11,00	- 11,80	- 11,20	- 11,20	- 9,50	- 11,00
dp/da, MPa/deg						
- 20	0,43	0,43	0,33	0,33	0,25	0,32
- 23	0,29	0,47	0,20	0,47	0,31	0,35
- 27	0,64	0,36	0,84	0,75	0,57	0,64

The values of crank angle fuel injection advance, presented in table 1, indicate on phenomena of inner catalyst impact on ignition delay. Combustion ignition is also related to engine speed: the higher engine speed the closer to TDC fuel combustion process starts.

The changes in pressure to crank angle ratio (dp/da), show that for 20 and 23 degrees of crank angle before TDC, the ratio values are higher when engine worked with platinum/rhodium catalyst on the engine valves surface in comparison to state without the engine modification (tab.1). Only for 27 deg of crank angle and the lower engine speed the relation was opposite. The phenomena needs to be explained in future researches.

The thermodynamic state of the medium in combustion chamber is determine by three parameters: pressure, temperature and volume. Two of them: pressure and volume as direct parameters are known as parameters indicates direct on engine performance. The third parameter, temperature, in engine measurements is define by mathematical rules because pressure and volume changes are easier and more precise tool for temperature measurement than using direct sensor of this parameter.

The maximum in-cylinder temperatures variation is shown on figures 3 and 4.

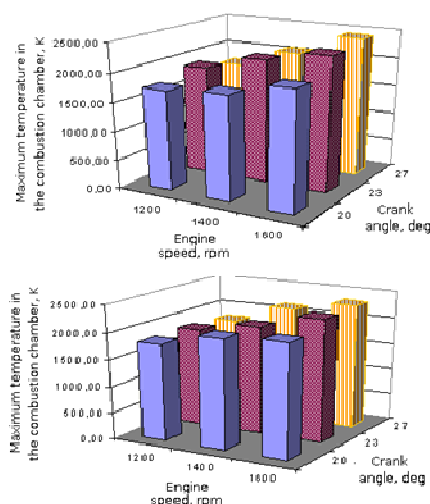


Fig. 3. The in-cylinder temperatures versus crank angle and engine speed, without (top) and with (down) inner catalyst application

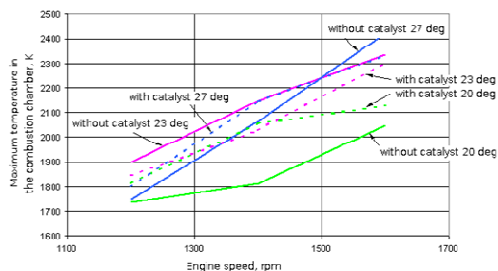


Fig 4. The in-cylinder temperatures versus engine speed, for both engine states (with and without catalyst) and various crank angle degrees

The results of in-cylinder temperature analysis indicates on effect of inner catalyst application on engine performance but trends of the engine parameters variations and their explanation should be investigate in the future research.

Polycyclic Aromatic Hydrocarbons

In result of the research eight from possible 16 hydrocarbons were detected: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pirene. The results of measurements are shown in the table 3.

Tab 3. PAHs concentration in the engine exhausts

PAH	Engine load, Nm	PAHs concentration [$\mu\text{g}/\text{dm}^3$] $\pm 30\%^{**}$			
		Without catalyst		With Pt catalyst	
		Idle run	30 Nm	Idle run	30 Nm
Naphthalene		0,0023	0,031	0,0069	0,027
Acenaphthylene		n.d.*	n.d.*	0,0032	0,00087
Acenaphthene		0,0032	0,011	0,0043	0,0048
Fluorene		0,014	0,012	0,0024	0,0032
Phenanthrene		n.d.*	n.d.*	n.d.*	n.d.*
Anthracene		0,035	0,035	n.d.*	n.d.*
Fluoranthene		n.d.*	0,0047	n.d.*	n.d.*
Pirene		0,0041	0,0084	n.d.*	0,0045
PAHs sum		0,059	0,10	0,017	0,041
Exhaust gases temp. K $\pm 1\text{K}$		432	482	507	568

Catalyst application in the combustion space causes changes in PAHs quantitative composition in both tested points of engine load (idle run and 30 Nm). What is important – the application of in-cylinder catalyst causes anthracene reduction, which toxicity is ten times higher than other identified PAHs (fig. 5).

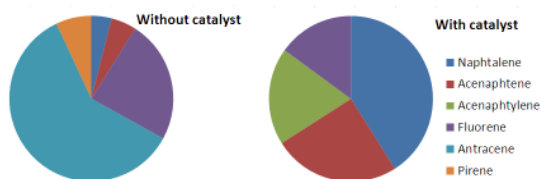


Fig. 5. Group PAHs share, % (12000 rpm, idle run)

In figure 6 (idle run) comparison of particular PAHs concentration and PAHs sum, before and after inert catalyst application, is shown.

Effectiveness of in-cylinder platinum-rhodium catalyst is more significant when engine is idle running (71%) than on higher load (59%)

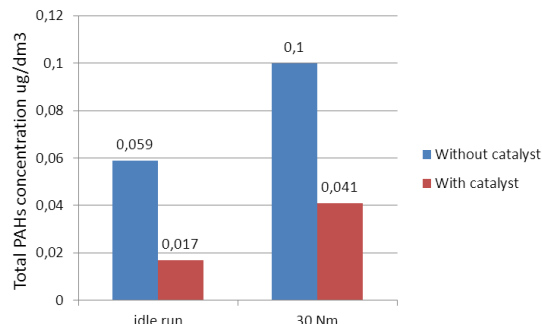


Fig 6. Total PAHs concentration in the exhaust with and without catalyst

PAHs sum reduction in both cases of engine loads is connected mainly with anthracene removing from exhaust and decrease of fluorene concentration.

Volatile Organic Compounds

The results of the experiment was VOC's quantity-quantitative analysis in function of chosen points of the engine work. The compounds from each VOCs groups (aldehydes, alcohols, ketones, aromatic hydrocarbons, paraffin hydrocarbons) was identified in the exhausts.

Platinum-rhodium active coating inside of the diesel engine caused significant decrease of total VOC's concentration on lower engine load (fig 7).

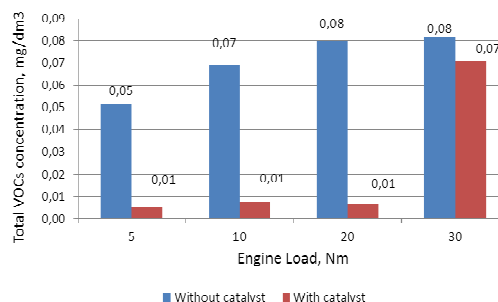


Fig 7. Total VOCs concentration in the exhaust with and without catalyst

The catalyst effectiveness is higher than 89 percent except the highest engine load (13 %). The situation is caused by some aldehydes generation (mostly low-toxic propionaldehyde) during the combustion process with active factor inside of the cylinder when engine was work with 30 Nm load. This phenomena need to be investigated in future researches.

6. Conclusions:

1. The platinum/rhodium active factor on zirconium thermal barrier coating placed into combustion chamber (inner catalyst) effects on the diesel engine performance.
2. The impact of the inner catalyst seems to be advantageous for ignition delay.
3. The active ceramic on the engine valve surface caused increase of in-cylinder maximum pressure and temperature values.
4. To determine and explain trends of pressure and temperature values changes versus engine parameters the researches on inner catalyst application should be continue and developed.
5. The inert catalyst application (active coating on research engine valves) is very advantageous for decrease of total polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs) concentration in engine exhaust gases, especially on idle run

Nomenclature/Skróty i oznaczenia

PAHs Polycyclic Aromatic Hydrocarbons
TBC Thermal Barrier Coating

VOCs Volatile Organic Compounds

Bibliography/Literatura

- [1] Siegla C.D., Plee S. L.: Heterogeneous Catalyst in the Diesel Combustion Chamber, *Combustion Science and Technology*, 1982, vol.27, pp 97-102
- [2] Johnes R.L. Catalytic Combustion Effects in Internal Combustion Engines, *Combustion Science and Technology*, 1997, vol.129, pp 185-195
- [3] Merkisz J., Pielecha J., Walkowiak W.. Wpływ modyfikacji świec żarowych na emisję związków toksycznych. W: *Rozruch silników spalinowych. Materiały sympozjum. Wydawnictwo Uczelniane. Szczecin 1998.*
- [4] Janicka A., Walkowiak W. W, Sobianowska-Turek A.: The impact of active ceramic coating implementation on gasoline engine exhaust toxicity. *Journal of KONES*. 2010, vol. 17, nr 3, s. 149-154
- [5] Sant-Georges F., Abbas I., Billet S., Verdin A., Gosset P., Mulliez P., Shirali P, Garcon G.: Gene expression induction of volatile organic compounds and/or polycyclic aromatic hydrocarbons – metabolizing enzymes in isolated human alveolar macrophages in response to airborne particulate matter (PM_{2,5}) *Toxicology* 244 (2008) 220-230
- [6] Williams K. A., Schmidt L.D.: Catalytic autoignition of higher alkane partial oxidation on Rh-coated foams, *Applied Catalysis A: General* 299 (2006), pp. 30-45
- [7] Mello J.P., Bezaire D., Sriramulu S.: Performance and Economics of Catalytic Glow Plugs and Shields in Direct Injection Natural Gas Engines for the Next Generation Natural Gas Vehicle Program; Final Raport, National Renewable Energy Laboratory, Cambridge, Massachusetts, August 2003, NREL/SR-540-34286

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