



## THE IMPACT OF PLATINUM-RHODIUM ACTIVE COATING INSIDE A COMPRESSION IGNITION ENGINE ON VOLATILE ORGANIC COMPOUNDS EMISSION

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### **Abstract**

*This paper presents the results of the researches on platinum-rhodium inner catalyst application in self-ignition engine (SB 3.1). A main aim of this study was volatile organic compounds (VOC's) marking in exhaust gases. Platinum and rhodium was used as an active coating. The catalyst was put onto the engine valves surface. As a catalyst support a zirconium ceramic was used. The ceramic layer was also used as a local thermal barrier. The results of the experiment was VOC's quantity-quantitative analysis in function of chosen points of the engine work. The results shows that platinum-rhodium active coating inside of the diesel engine caused about tenfold total VOC's concentration decrease. Because of significant toxicity of benzene and formaldehyde, for those compounds separate comparison analysis was done. Decrease of benzene concentration was also observed but catalyst effectiveness was lower than for total VOC's concentration. The results of analysis of the catalyst influence on formaldehyde concentration in exhaust are ambiguous.*

*Keywords: combustion engines, inner catalyst, volatile organic compounds, exhaust toxicity*

### **1. Introduction**

Several anthropogenic activities lead to volatile organic compounds emission into the atmosphere. One of the most important is motorization. VOC's emitted from combustion engines are very often hazardous compounds for human and environment [1, 3-5]. In the atmosphere, VOC's contribute to tropospheric ozone formation, stratospheric ozone layer depletion and to the greenhouse effect [3]. Inside the human body this organic compositions are able resolve in fat and to cumulate in tissues.

Volatile organic compounds are significant group amid 200 identified compounds in diesel engine exhaust (mainly aldehydes but also alcohols, ketons, esters, paraffin and aromatic hydrocarbons). In group of VOC's the most toxic and common in human environment are particularly: benzene, formaldehyde (methanal) and acrolein [5].

### **2. Experiment**

A modified SB3.1. compression ignition engine (diesel engine) was employed as a research engine. An engine modification was application of platinum-rhodium coating on engine valves. Conventional fuel (commercial diesel oil) was used as engine fuel. SB3.1 engine was loaded

with Hengan-Froude engine break. The most characteristic points of functional engine work (rotation speeds and loads) was chosen in experiment: 1200 r.p.m., engine loads: 5 Nm, 10 Nm, 20 Nm, 30 Nm and 1600 r.p.m., engine loads: 10 Nm, 20 Nm, 30 Nm (it was not possible to stabilize engine work for 5 and 30 Nm in initial conditions and 5 Nm when engine working with catalyst on the engine valves).

An engine modification was based on application of platinum-rhodium active coating on surface of the engine valves. Zirconium ceramic was used as a catalyst support.

A scheme of research work stand – engine test house – is presented in the figure 1.

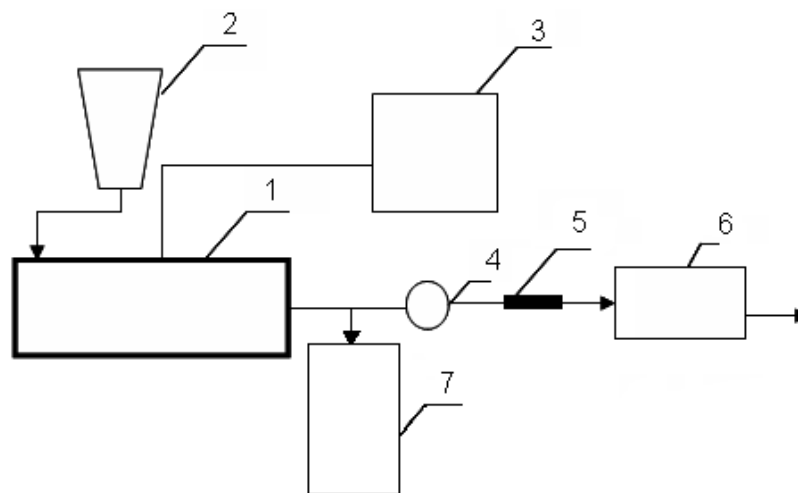


Fig. 1. Research workstand: engine test house. 1 – engine with a break, 2 – fuel reservoir, 3 – NO, CO and smoke level analyzers, 4 – formaldehyde absorber, 5 – tube with active coal, 6 – exhaust gases uptake system, 7 – engine control system

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. Carbene disulfide ( $CS_2$ ) was used for VOC's extraction from active coal. Gas chromatograph Hewlett-Packard 5890 with FID detector and capillary column (HP-5, 30 m, 0,53 mm) was used for quantity and quality analysis. The chromatography conditions were: column temperature (110 °C), dozers (150 °C) and detectors (250 °C).

### 3. Results and discussion

The results of the experiment was VOC's quantity-quantitative analysis in function of chosen points of the engine work.

The VOC's concentration,  $mg/dm^3$ , during engine work without catalytic coating application on engine valves is presented in table 1.

Tab. 1. Volatile Organic Compounds concentration in SB 3.1 engine gases. Initial conditions (engine without catalyst). Benzene and formaldehyde concentration is presented also separately because of its separate analysis in function of chosen points of engine work

Engine speed	1200 , r.p.m.				1600 , r.p.m.	
Engine load, Nm	5	10	20	30	10	20
VOC's groupe name	Concentration , $mg/dm^3$ *					
Aldehydes	0,042	0,059	0,061	0,061	0,059	0,086

Alcoholes	0,0066	0,0064	0,0054	0,0051	0,0066	0,0058
Ketons	n.d.**	n.d.**	0,0075	0,0009	0,015	n.d.**
Aromatic hydrocarbons	0,0027	0,0034	0,0052	0,010	0,0060	0,0064
Praffin hydrocarbons	n.d.**	n.d.**	0,00028	0,0045	0,0049	0,0044
<b>Total VOC's</b>	<b>0,051</b>	<b>0,069</b>	<b>0,080</b>	<b>0,081</b>	<b>0,091</b>	<b>0,10</b>
Benzene	0,0014	0,0022	0,0015	0,0028	0,0012	0,0018
Formaldehyde	0,0032	0,0039	0,0043	0,0044	0,0040	0,010

\* the total method relative error is estimated on 20 % level

\*\* non detected

Total VOC's concentration is presented on figure 2. It is shown that with engine speed and engine load also volatile compounds emission is rising.

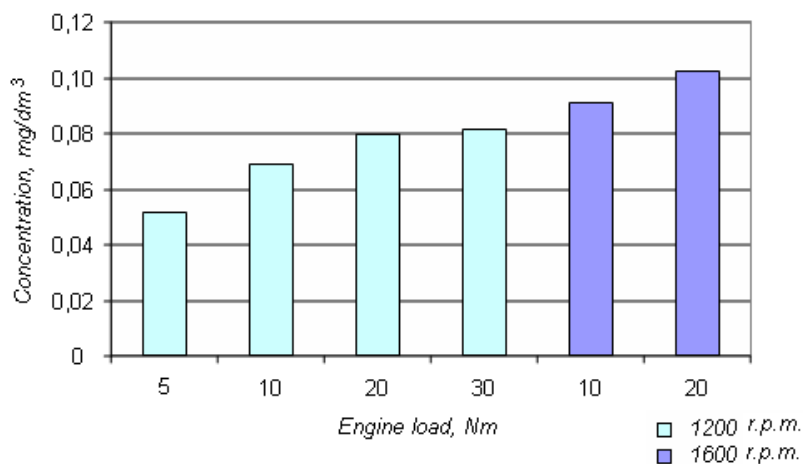


Fig. 2. Total VOC's concentration in SB 3.1 engine gases (initial conditions – engine without catalyst)

On following figures benzene (figure 3) and formaldehyde (figure 4) concentrations in function of engine work is shown.

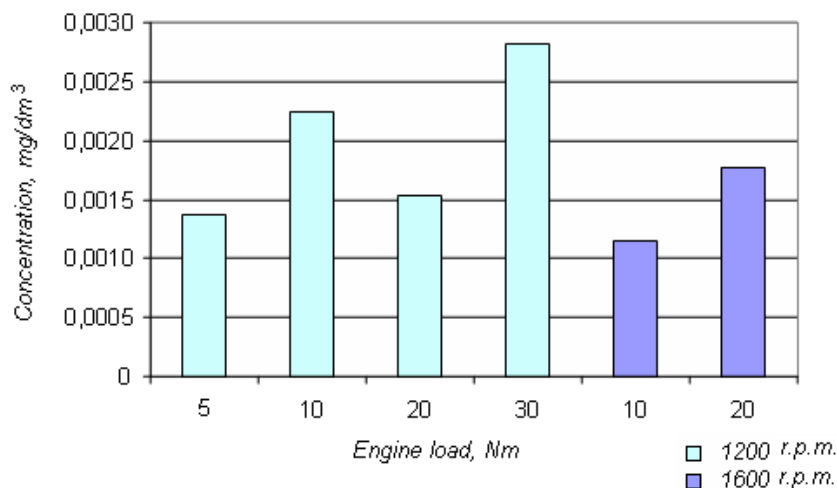


Fig. 3. Benzene concentration in SB 3.1 exhausts (initial conditions – engine without catalyst)

The lowest benzene concentration ( $0,0012 \text{ mg/dm}^3$ ) was observed when engine was working with 10 Nm load and higher rotational speed and the highest concentration ( $0,0028 \text{ mg/dm}^3$ )

was detected for lower rotational speed and engine load 30 Nm. Benzene emission seems to rise proportional to engine load for both engine speeds but the results are ambiguous.

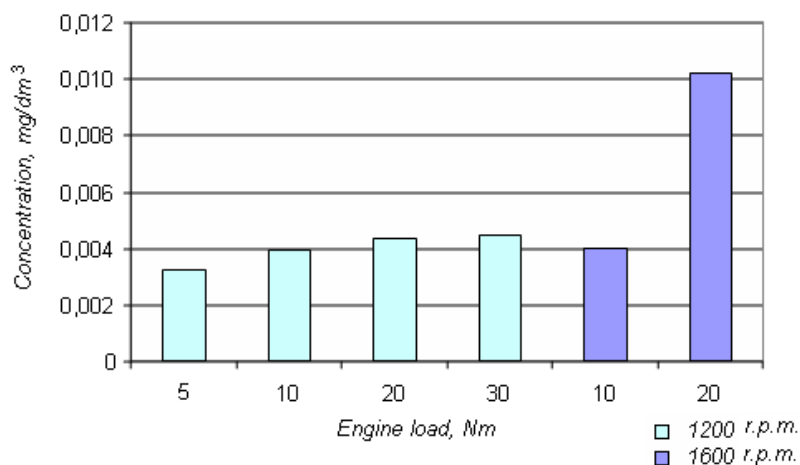


Fig. 4. Formaldehyde concentration in SB 3.1 exhausts (initial conditions – engine without catalyst)

In case of formaldehyde, insignificant concentration increase with engine load was observed when engine was working with lower engine speed. When engine was working with 1600 r.p.m. concentration of this compound rise rapidly (over 250 %) when engine load increase from 10 Nm to 20 Nm.

The results of VOC's analysis for the engine with platinum-rhodium active coating on the engine valves are presented in table 2.

Tab. 2. Volatile Organic Compounds concentration in SB 3.1 engine . Engine without catalyst (Pt/Rh active coating on the engine valves surface). Benzene and formaldehyde concentration is presented also separately because of its separate analysis in function of chosen points of engine work

Engine speed	1200 , r.p.m.				1600 , r.p.m.		
Engine load, Nm	5	10	20	30	10	20	30
VOC's groupe name	Concentration , mg/dm <sup>3</sup> *						
Aldehydes	0,00058	0,00202	0,00535	0,07085	0,00579	0,02904	0,01888
Alcholes	0,00346	0,00153	0,00175	0,00089	0,00102	0,00142	0,00061
Ketons	n.d.**	0,00086	0,00048	0,00068	n.d.**	n.d.**	n.d.**
Aromatic hydrocarbons	0,00127	0,00292	0,00137	0,00198	0,00208	0,00662	0,00114
Praffin hydrocarbons	0,00028	0,00067	0,00031	0,00079	n.d.**	0,00025	0,00021
<b>Total VOC's</b>	<b>0,006</b>	<b>0,008</b>	<b>0,009</b>	<b>0,075</b>	<b>0,009</b>	<b>0,037</b>	<b>0,021</b>
Benzene	0,00095	0,00208	0,00096	0,00150	0,00085	0,00110	0,00114
Formaldehyde	n.d.**	0,00060	0,00500	0,00934	0,00320	0,02540	0,01660

\* the total method relative error is estimated on 20 % level

\*\* non detected

Total volatile organic compounds concentration in this condition of engine work (figure 5) seems to be on similar level (about 0,007 mg/dm<sup>3</sup>) for first three engine loads (engine speed 1200 r.p.m.). When engine worked with load 30 Nm total VOC's concentration increased tenfold. It is correlated with tenfold increase of aldehydes concentration in exhausts.

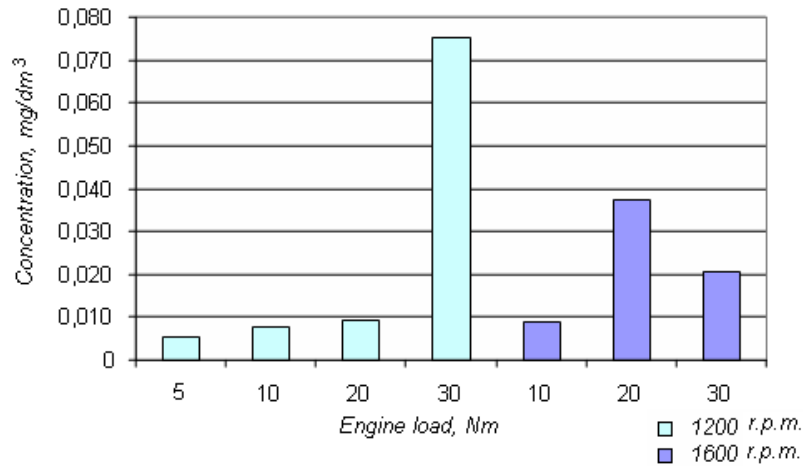


Fig. 5. Total VOC's concentration in SB 3.1 exhaust gases (engine with catalyst)

Benzene concentration in exhausts in engine load function is presented on figure 6.

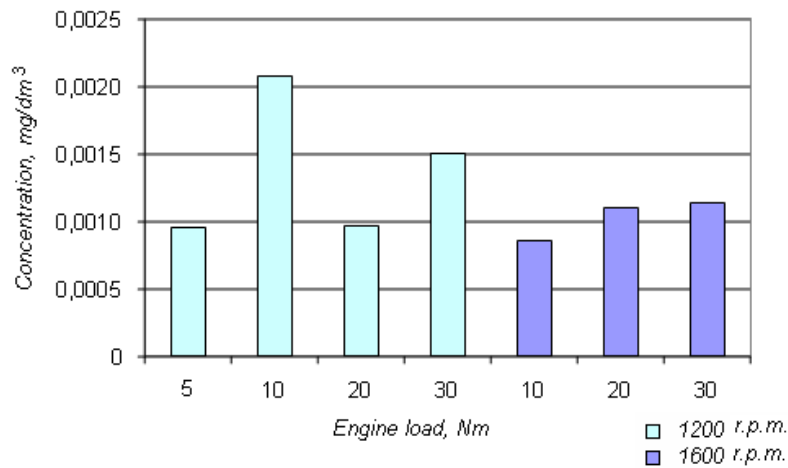


Fig. 6. Benzene concentration in SB 3.1 exhausts (engine with catalyst)

Lower benzene concentration was observed when engine was working with higher engine speed. Despite the fact that benzene concentration for 1600 r.p.m. was lower than for 1200 r.p.m. it was increasing with engine load. When engine was working with 1200 r.p.m. benzene concentration was changing rapidly and without unambiguous trend.

On figure 7 formaldehyde concentration in engine load function is presented.

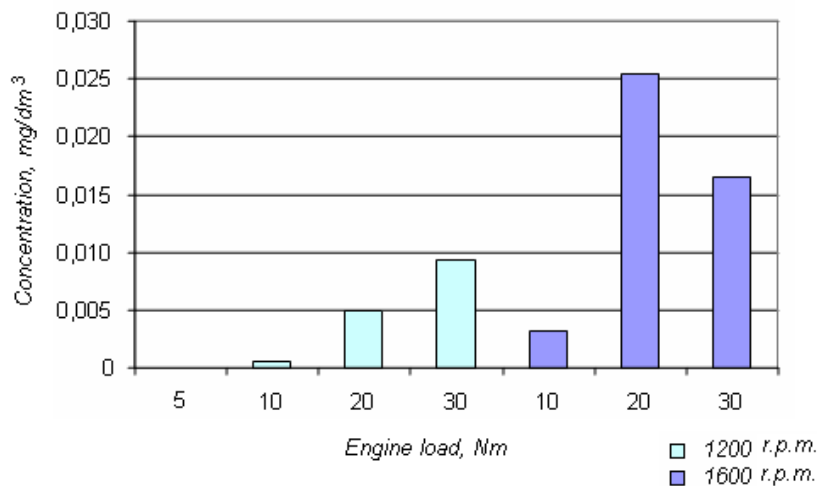


Fig. 7. Formaldehyde concentration in SB 3.1 exhausts (engine with catalyst)

For engine speed 1200 r.p.m. formaldehyde concentration was significant increasing with engine load. When engine was working with higher rotational speed concentration increasing in engine load function was also observed but the highest concentration was detected when engine worked with 20 Nm load.

For effectiveness estimation of active coating application inside diesel engine a comparison total VOC's concentration in engine exhaust gases in both conditions (engine with and without catalyst) was done (figure 8).

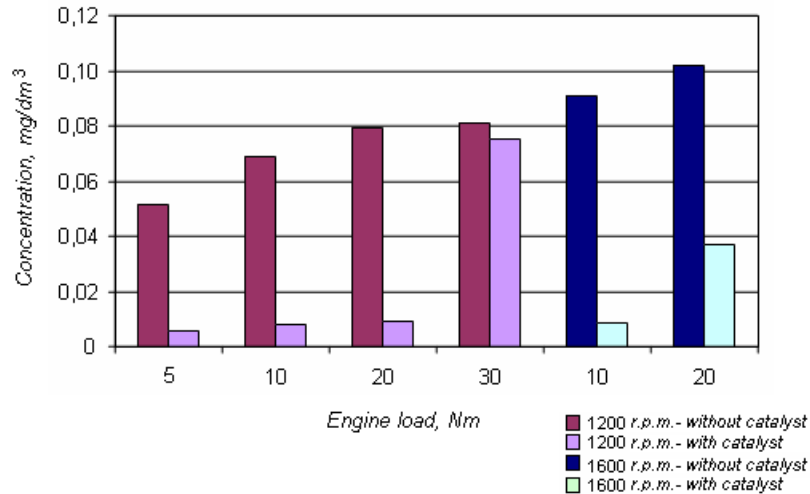


Fig. 8. Comparison of total VOC's concentration in exhausts for both condition: engine with and without catalyst in function of engine work

Platinum-rhodium active coating inside of the diesel engine caused about tenfold total VOC's concentration decrease. Because of significant toxicity of benzene and formaldehyde for those compounds separate comparison analysis was done.

On figure 8 benzene concentration for both conditions of engine work in function of engine work is presented. Decrease of benzene concentration when engine was working with catalyst is observed in every point of engine work but catalyst effectiveness is lower than for total VOC's concentration (figure 9).

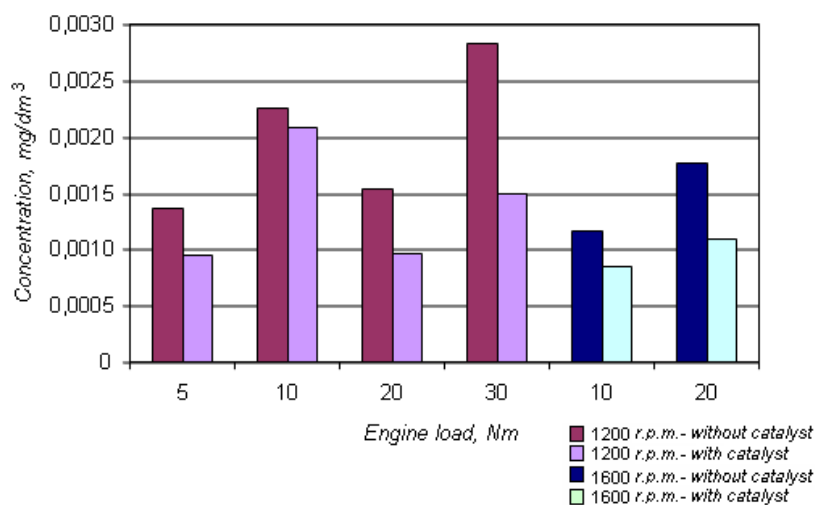


Fig. 9. Comparison of benzene concentration in exhausts for both condition: engine with and without catalyst in function of engine work

For formaldehyde decrease of concentration level when engine was working with catalyst was also observed (except two points of engine work: 1200 r.p.m./30 Nm and 1600 r.p.m./20 Nm) (figure 10).

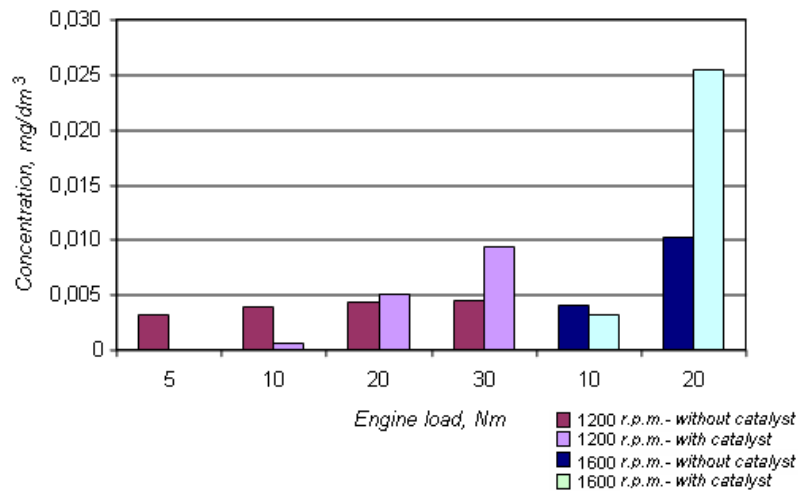


Fig. 10. Comparison of formaldehyde concentration in exhausts for both condition: engine with and without catalyst in function of engine work

Those two points of engine work are maximum engine load in case of both engine speeds. In this points the highest temperature of exhausts was observed. For catalytic process the temperature level is very important (it influence on effectiveness of the process) that's why a complete analysis of VOC's concentration in function of various values in needed.

#### 4. Conclusions:

1. Platinum-rhodium active coating inside of the diesel engine (on the engine valves surface) caused about tenfold total VOC's concentration decrease and significant decrease of the most toxic substances (from VOC's identified in the engine exhaust gases): benzene and formaldehyde.
2. Because of ambiguous results of some stages of the experiment complete analysis of VOC's concentration in function of various values in needed.

#### References:

- [1] Czarny A, Zaczyńska E, Mendyka B., Janicka A., *Influence of biodiesel exhaust on NF-κB activation and TNF-α production in human lung and peripheral blood leukocytes, in vitro*. Materiały Konferencyjne IV Konferencja Naukowo-Szkoleniowa "Immunomodulacja: badania doświadczalne i kliniczne". Jurata, Polska, 25.05.-26.05 2007.
- [2] Fishader G., roder-stolinski C., Wihmann G., Nieber K., Lehmann I., *Release of MCP-1 and IL-8 from lung epithelial cells exposed to volatile organic compounds*. Toxicology in Vitro 22 (2008) 359-366.
- [3] Janicka A., Walkowiak W, Szczepaniak W., *Inert catalyst in compression ignition engine. VOC's emission*, Journal of KONES Powertrain and Transport vol.14, No.5./2007.
- [4] Janicka A., Walkowiak W., *Emisja lotnych związków organicznych i wielopierścieniowych węglowodorów aromatycznych z silnika zasilanego biopaliwem*. Silniki Spalinowe. 2007 R. 46, nr SC3.
- [5] Lebrecht G., Czerczak S., Szymczak W., *Benzen – dokumentacja*. Podstawy i Metody Oceny Środowiska Pracy Numer 1 (35) 2003.