

# THE EFFECT OF PT ACTIVE COATING APPLICATION INSIDE DIESEL ENGINE ON POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) EMISSION

**Anna Janicka**

*Wroclaw University of Technology, Institute of Environmental Protection Engineering  
Wybrzeże Wyspiańskiego 27, 50-370 Wroclaw, Poland  
tel.: +48 94 3478344, fax: +48 94 3426753  
e-mail: anna.janicka@pwr.wroc.pl*

**Wojciech Walkowiak**

*Wroclaw University of Technology, Institute of Machine Design and Operation  
Wybrzeże Wyspiańskiego 27, 50-370 Wroclaw, Poland  
e-mail: wojciech.walkowiak@pwr.wroc.pl*

**Włodzimierz Szczepaniak**

*Wroclaw University of Technology Institute of Environmental Protection Engineering  
Wybrzeże Wyspiańskiego 27, 50-370 Wroclaw, Poland  
e-mail: wlodzimierz.szczepaniak@pwr.wroc.pl*

## **Abstract**

*Application of active coating inside of an self-ignition engine may have an important impact on several stages of combustion process: fuel cracking, fore-flame phase, combustion phase and secondary combustion phase [7]. Investigations of such construction are very rare in the literature - especially of hydrocarbons emission. Polycyclic aromatic hydrocarbons (PAHs) are known to have mutagenic and carcinogenic effect on humans [2, 6, 7]. One of the most important anthropogenic source of these substances is motorization (especially diesel engines). The paper presents results of measurements of PAHs emissions from SB3.1 self-ignition engine with Pt active coating application inside. The catalyst was applied on engine valves surface. Zirconium ceramic was chosen as a coating for catalyst application (also because of its thermo-insulating properties). Because of unstable parameters of self-ignition engine work (pressure and temperature jumps), PAHs were extracted from two phases: gas phase and solid phase (particle matter - PM). A chromatographic method of PAHs identification and analysis, because of their low level of concentration in exhaust gases, needed to be supported by sample purification and enrichment stages [40]. It has been found that a significant decrease of total toxic polycyclic aromatic hydrocarbons concentration in engine exhaust gases for engine with Pt catalyst application. The catalyst application causes also changes in relative concentrations of polycyclic aromatic hydrocarbons.*

**Keywords:** *active coating, catalyst, polycyclic aromatic hydrocarbons, diesel engine*

## **1. Introduction**

Self-ignition engine exhausts consist over 100 individual hazardous chemical components that when combined, can result in as many as 10000 chemical compounds. According to International Agency for Research on Cancer (IARC) a large majority of these compounds are listed as being cancer causing or suspected carcinogenic [2]. Diesel emissions have been considered a potential health hazard, mainly because it contains carcinogenic hydrocarbons like PAHs (polycyclic aromatic hydrocarbons) [1]. As an effective method for controlling emissions of PAHs from diesel engine the catalytic combustion has been proposed and developed. Precious metals like platinum,

palladium, ruthenium, rhodium or oxides of such metals as manganese, chromium and copper are usually used as combustion catalyst of hydrocarbons. The catalysts are deposited on monolith supports and placed into vehicle exhaust system as catalytic reactors. Their effectiveness is correlated with exhaust gases temperature and reaches the highest values when exhaust gases temperature is between approximately 520 and 570 K. When engine is idle running exhaust gases temperature is too low to ensure sufficient effectiveness of catalytic reactor in reduction of CO and hydrocarbons (HC) [3, 5].

## 2. Experimental

A modified SB3.1 self-ignition engine (diesel engine) was used as a research engine with engine modification consisted in application of platinum catalyst on engine valves. Zirconium ceramic was used as a catalyst support layer. A scheme of the inner catalyst is shown in the Fig. 1.

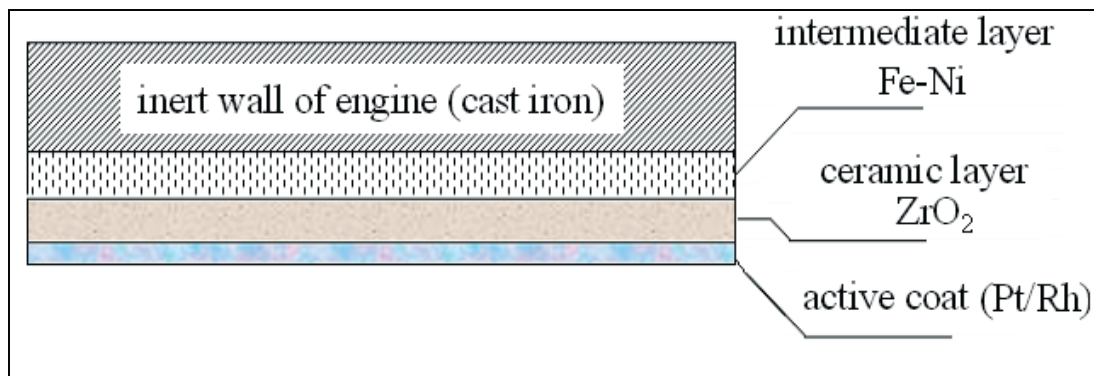


Fig. 1. Scheme of the inner catalyst

Conventional fuel (commercial diesel oil) was used as engine fuel. Two characteristic engine loads: idle run and 30 Nm, were chosen. PAHs emission control was a main aim of the present investigation. A scheme of research work stand - engine test house - is presented in the Fig. 2.

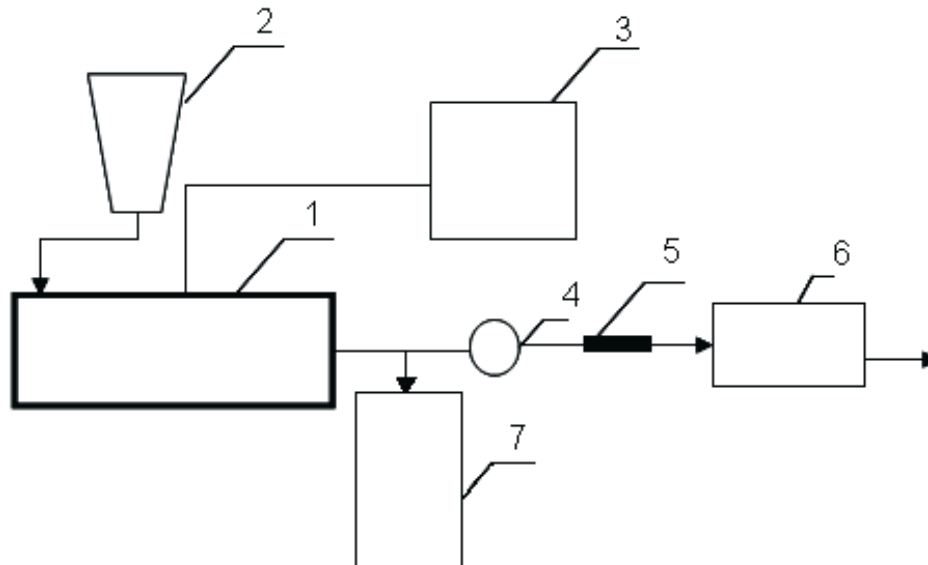


Fig. 2. Research workstand: engine test house: 1-engine with a break, 2 - fuel reservoir, 3 - NO, CO and smoke level analyzers, 4 - filter, 5 - tube with active coal, 6 - exhaust gases uptake system, 7 - engine control system

Analysis procedure of PAHs concentration in exhaust gases was consisted of 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 uptaken 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 (SPE) was used for samples purification. 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. Calibration of the chromatograph 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 [4].

## 2. Results and discussion

Only seven from possible 16 hydrocarbons was detected during present investigations: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pirene Results of measurements are shown in the Tab. 1.

Tab. 1. Polycyclic aromatic hydrocarbons concentration [ $\mu\text{g}/\text{dm}^3$ ] and exhaust gases temperature in diesel engine exhaust gases in two states of engine work

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
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] $\pm$ 1K		432	482	507	568

\* - non detected \*\* method error

Application of engine valves with catalyst on zirconium ceramic support causes significant increase of exhaust gases temperature:  $\sim$  75 K when engine was idle running and  $\sim$  86 K on load 30 Nm. This phenomenon may be connected with improvement of combustion process (active agent which is put into combustion space causes the start of complicated chain reactions, which is related with shortening of time of chemical autoignition delay [6,7]) but also because the ceramic layer application which was used as a catalyst support acts as a thermo-insulating material (thermal barrier)).

Catalyst application in the combustion space results in PAHs quantitative composition change in both cases of engine load (idle run and 30 Nm). When engine was idle running without catalyst anthracene (60%), fluorene (24%), pirene (7%), acenaphthene (5%) and naphthalene (4%) were identified. After catalyst application on engine valves naphthalene (41%), acenaphthene (25%) and

fluorene (15%) were detected, Appearance of acenaphtylene were observed at qualitative level, anthracene and pirene weren't identified (Fig. 3)

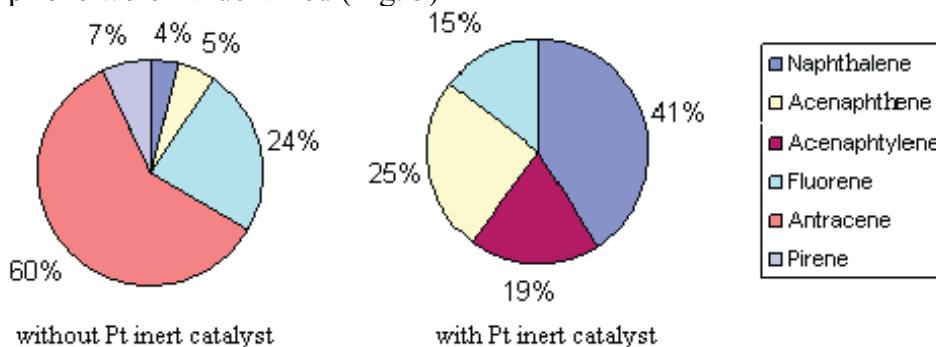


Fig. 3. Share of particular PAHs in their sum. Idle run

When engine worked on load 30 Nm without catalyst anthracene (34%) naphthalene (30%), fluorene (12%), acenaphthene (11%), pirene (8%), fluoranthene (5%) were detected. After catalyst application anthracene wasn't identified and appearance of acenaphtylene (2%) was observed (like when engine was idle running). Increase of naphthalene (67%) share in PAHs sum was also observed.

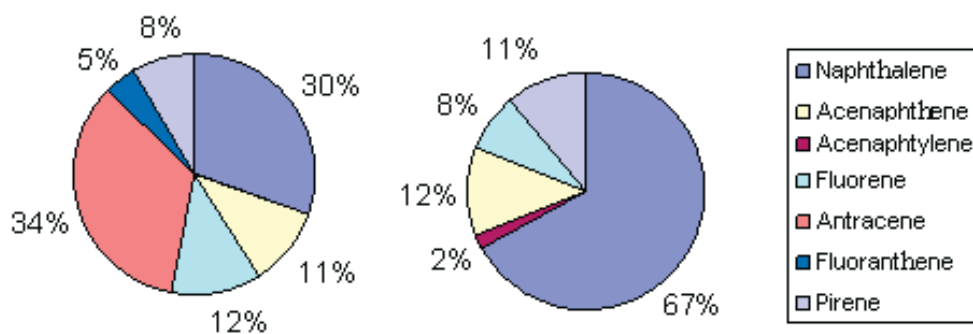


Fig. 4 Share of particular PAHs in their sum. Engine load: 30Nm

Comparison of particular PAHs concentrations and PAHs sum, before and after inner catalyst application, is shown on Fig. 5 (idle run) and Fig. 6 (engine load: 30Nm). PAHs sum reduction in both cases of engine load was connected mainly with anthracene removing from exhaust gases and decrease of fluorene concentration.

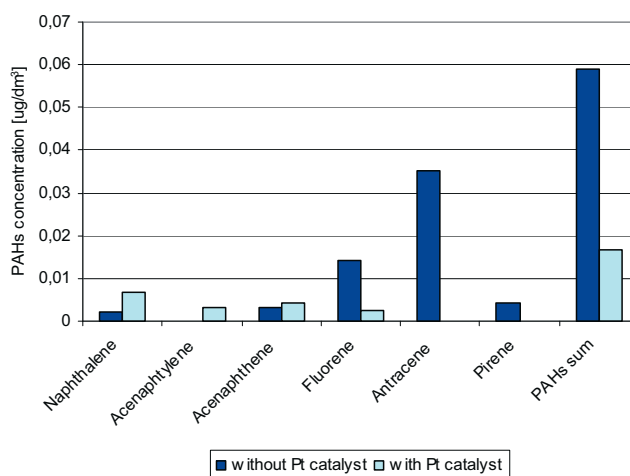


Fig. 5 Share of particular PAHs in their sum. Engine load: 30 Nm

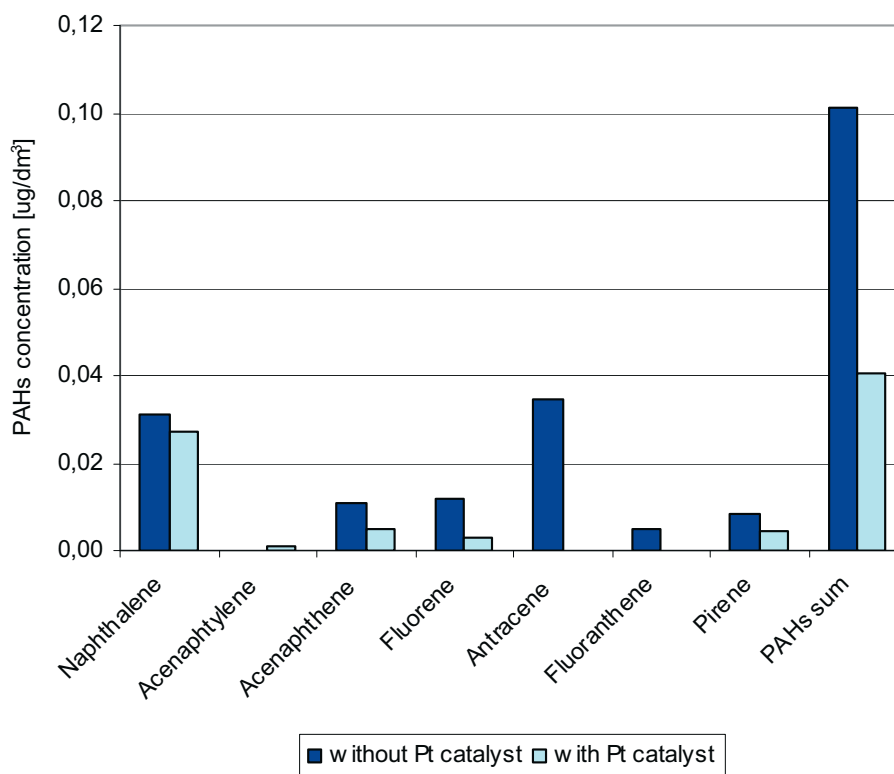


Fig. 6 PAHs concentration [ $\mu\text{g}/\text{dm}^3$ ] in exhaust gases. Engine Load: 30 Nm

Efficiency of PAHs reduction with Pt inner catalyst varied from 60% at engine load of 30 Nm to 71% when engine was idle running.

#### 4. Conclusions

1. The inner catalyst application (active coating on research engine valves) is efficient in decreasing of total polycyclic aromatic hydrocarbons (PAHs) concentration in engine exhaust gases, especially on idle run.
2. The inner catalyst application causes changes in relative concentrations of polycyclic aromatic hydrocarbons.
3. The decrease of the sum of PAHs concentration is connected mainly with anthracene removing from exhausts and decrease of fluorene concentration.

#### References

- [1] Dobbins, R. A., Fletcher, R. A., Benner, B. A., Hoefft, S., *Polycyclic aromatic hydrocarbons in flames, in diesel fuels and in diesel emissions*, Combustion and flame 144 (2006). pp. 773-781.
- [2] Kuo, C. Y., Hsu, Y. W., Lee, H. S., *Study of Human Exposure to Particulate PAHs Using Personal Air Samplers* Arch. Environ. Contam. Toxicol., 44, pp. 454-459 (2003).
- [3] 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 Report, National Renewable Energy Laboratory, Cambridge, Massachusetts, August 2003, NREL/SR-540-34286.
- [4] Mendyka, B., Syczewska, K., *Optimalizacja metody przygotowania próbki WWA do analizy chromatograficznej z różnych elementów środowiska*, Raport Politechniki Wrocławskiej serii SPR Nr 26/99.

- [5] Musialik - Piotrowska, A., Syczewska, K., Mendyka, B., *Katalityczne spalanie wielopierścieniowych węglowodorów aromatycznych*, Instytut Inżynierii Ochrony Środowiska Politechniki Wrocławskiej, Raport serii SPR Nr 2/97.
- [6] Rhead, M. M., Hardy, S. A., *The sources of polycyclic aromatic compounds in diesel engine emission*, Fuel 82 (2003), pp. 385-393.
- [7] Walkowiak, W. i in, *Obniżanie toksyczności spalin silnika o zapłonie samoczynnym przez zastosowanie wewnętrznego katalizatora spalania*, Raport Politechniki Wrocławskiej Seria, Spr 47/2007.