THE EFFECT OF Pt INTERNAL CATALYST ON RELATIVE CARCINOGENIC COEFFICIENT (RCC) OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) EMITTED FROM DIESEL ENGINE

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Abstract

One of the main anthropogenic sources of PAHs emission is motorization, especially compression ignition engines. The researches of International Agency for Research on Cancer (IARC) proved that some compounds from polycyclic aromatic hydrocarbons group are toxic for live organisms and cause damages of adrenal glands, lymphatic, circulation and respiratory systems. Because of carcinogenic properties and common occurrence in human environment benzo(a)pirene has been accepted as polycyclic aromatic hydrocarbons indicator. In relation to benzo(a)pirene, Nisbet and LaGoy determined relative carcinogenic coefficients (RCC) for individual polycyclic aromatic hydrocarbons. The paper presents results of analysis of PAHs RCC emitted 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-isolating 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 polycyclic aromatic hydrocarbons identification and analysis, because of their low level of concentration in exhaust gases, needed to be supported by sample purification and enrichment stages. It has been found that implementation of catalytic coating on valves of the engine causes decrease of polycyclic aromatic hydrocarbons concentration in exhaust gases, what results in decrease (in most cases) of the sum of relative carcinogenic coefficient of polycyclic aromatic hydrocarbons.

Keywords: *internal catalyst, polycyclic aromatic hydrocarbons, relative carcinogenic coefficient, diesel engine*

1. Introduction

Urban areas, especially mega-cities have suffered from the serious air pollution problem. The largest source of pollution in most urban areas is motor vehicles. A recent study estimated that approximately 64000 people in the United States die from heart or lung disease every year because of air pollution (more people than die each year in car accidents) [1]. This rapid growth rate, compared with recent epidemiological studies, creates new public health concerns.

The most important group of substances from motorization source which are known to have mutagenic and carcinogenic effect on humans are polycyclic aromatic hydrocarbons (PAHs) (their main source are diesel engines).

2. Estimation of PAHs toxicity

The methods of investigation of substance toxic activity can be general divided as [2]:

- estimation of substance toxicity based on relation between chemical structure of substance and its biological activity (new direction of toxicology science),
- investigation of substance toxicity based on tests on animals (the most popular method)
- alternative methods based on rule 3R (replacement, reduction, refinement) which aim is to eliminate or reduce of animal suffer.

Concentration toxicometry investigations are usually applied to determine safe for humans level of the substance (the quantitative assessment of toxicity and hazards of potentially toxic substances).Concentration limits of potential toxic substances have various applications. The most popular are [2]:

- recommended Maximum Concentration Limit (RMCL) for air and workstand, averaged for various time periods,
- allowable Daily Intake (ADI),
- allowable Week Intake (AWI).

For toxicity estimation and analysis of the group of substances usually data for one representative and common compound occurring in environment are used (i.e. benzo(a)pirene for PAHs). The intensity of mutagenic, carcinogenic, irritant or sensitize activity of other compounds from the group is counted in relation to the representative compound. This method can be used to determinate Relative Toxicity (mutagenic, carcinogenic, irritant or sensitize) Coefficient (RTC) for all substances from the group. RTC can be evaluated on the bases of empirical or modeling researches. The Relative Carcinogenic Coefficients (RCCs) for polycyclic aromatic hydrocarbons determined by different authors are shown in Tab. 1.

Tab. 1. Relative Carcinogenic Coefficients (RCC) determined by difference authors

No.	PAH	EPA [3] (1984)	Chu i Chen [4] (1984)	Clemens [4] (1986)	Thorslund [5] (1990)	Nisbet i LaGoy [6] (1992)
1	Naftalene	0	n.d.*	n.d.*	n.d.*	0.001
2	Acenaphthalene	0	n.d.*	n.d.*	n.d.*	0.001
3	Acenaphthene	0	n.d.*	n.d.*	n.d.*	0.001
4	Fluorene	0	n.d.*	n.d.*	n.d.*	0.001
5	Fenantrene	0	n.d.*	n.d.*	n.d.*	0.001
6	Antracene	0	n.d.*	0.32	n.d.*	0.010
7	Fluoranthene	0	n.d.*	n.d.*	n.d.*	0.001
8	Piren	0	n.d.*	0.0810	n.d.*	0.001
9	Benzo(a)antracene	1	0.0130	0.1450	0.1450	0.100
10	Chryzene	1	0.0010	0.0044	0.0044	0.010
11	Benzo(j.b)fluoranthene	1	0.0800	0.1400	0.1200	0.100
12	Benzo(k)fluoranthene	1	0.0040	0.0660	0.0520	0.100
13	Benzo(a)pirene	1	1	1	1	1
14	Indeno(1.2.3-cd)pirene	1	0.0017	0.2320	0.2780	0.1
15	Dibenzo(a.h)antracene	1	0.6900	1.1000	1.1100	1
16	Benzo(ghi)perylene	0	n.d*	0.0220	0.0210	0.010
* n.d. – no data						

In recent researches [7-11] on PAHs RCC determinated mainly by Nisbet and LaGoy with modeling method based on toxicology experiments were used.

2. Simulation of start up of the vehicle with a combustion engine

A modified SB3.1 self-ignition engine (diesel engine) was used as a research engine. A scheme of research work stand - engine test house - is presented in the Fig. 1.

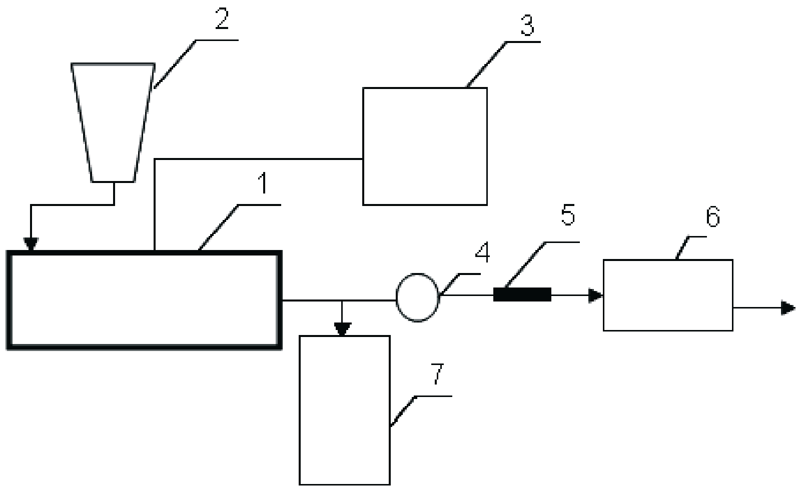

Fig. 1. Research workstand: engine test house:1-engine with a break, 2-fuel reservoir, 3-NO. CO and smoke level analyzers, 4-filter, 5-tube with active coal, 6-exhaust gases uptake system, 7-engine control system

An engine modification was based on application of platinum catalyst on engine valves. Zirconium ceramic was used as a catalyst support layer. A view of SB3.1 engine valves with inner catalyst is shown in the Fig. 2.

Fig. 2. The SB3.1 engine valves: with ceramic layer (on left) and with ceramic layer coated platinum

Conventional fuel (commercial diesel oil) was used as engine fuel. Two characteristic engine loads: idle run and 150 Nm. were chosen. PAHs emission control was a main aim of the present investigation. For estimation of exhaust toxicity Nisbet and LaGoy Relative Carcinogenic Coefficients (RCC) was used (Tab. 1).A scheme of the internal catalyst and a description of PAHs marking method in engine exhaust is presented in simultaneous published paper "The effect of Pt active coating application inside diesel engine on polycyclic aromatic hydrocarbons (PAHs) emission" (Journal of Kones 2008. related paper). (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 ^{o}C with 15 deg/min increase [4].

3. Results and discussion

As the result of our investigations 7 from possible 16 compounds was identified (Tab. 2). Except antracene all detected PAHs were characterized by RCC level of 0.001. RCC for antracene is tenfold higher (0.01).

*Tab. 2. PAHs detected in exhausts of research diesel engine (*with and without inner catalyst)

PAH name	RCC according to Nisbet and LaGoy [ ]	Without catalyst		With catalyst	
		Engine load			
		Idle run	30 Nm	Idle run	30 Nm
Naphthalene	0.001	+	+	+	+
Acenaphthylene	0.001	-	-	+	+
Acenaphthene	0.001	+	+	+	+
Fluorene	0.001	+	+	+	+
Antracene	0.01	+	+	-	-
Fluoranthene	0.001	-	+	-	-
Pirene	0.001	+	+	-	-

Tab. 1. Relative Carcinogenic Coefficients (RCC) determined by difference authors. (+) identified. (-) non detected

The relative carcinogenic coefficients for total PAHs identified in exhaust gasses have been determinated (Tab. 3).

Tab.3. Relative carcinogenic coefficients (RCCs) of total PAHs emitted from SB3.1 diesel engine.

	Without catalyst		With Pt internal catalyst	
	Idle run	30 Nm	Idle run	30 Nm
Total PAHs concentration [µg/dm^3]	0.059	0.10	0.017	0.041
RCC	0.00038	0.00041	0.00002	0.00004

Inner catalyst application caused total PAHs concentration decrease. High effectiveness of the reduction of total PAHs concentration was observed: from 60% (when engine worked with load 30 Nm) to almost 73% (when engine was idle running) but effectiveness of PAHs RCC reduction was even higher (from 90-95%) (Fig. 3).

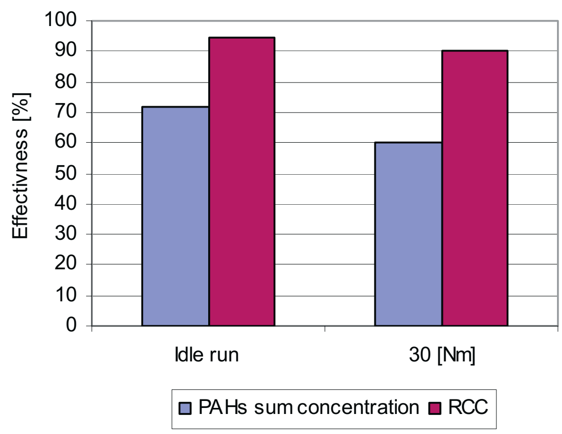

Fig. 3. Effectivness [%] of reduction of relative carcinogenic coefficient (RCC) for total PAHs and PAHs concentration emitted by SB3.1 self-ignition engine with Pt inner catalyst application

Effectiveness of PAHs RCC reduction is connected with antracene removing from exhausts. When engine worked without inner catalyst antracene constituted 60% share in PAHs sum on idle run and 34% on 30 Nm engine load. After inner catalyst application complete reduction of antracene was observed. As mentioned above. RCC for antracene is tenfold higher then for other identified polycyclic aromatic hydrocarbons what explains so high effectiveness of PAHs RCC reduction when engine worked with Pt catalyst.

4. Conclusions

1. The inner catalyst application (active coating on research engine valves) is efficient in decreasing of total polycyclic aromatic hydrocarbons (PAHs) relative carcinogenic coefficient (RCC) in engine exhaust gases. especially on idle run.
2. The decrease of RCC for total PAHs is connected mainly with antracene removing form exhausts.

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