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THE EFFECT OF PLATINUM-RHODIUM INNER CATALYST APPLICATION IN A COMPRESSION IGNITION ENGINE ON TOXICITY EQUIVALENT FACTOR OF VOLATILE ORGANIC COMPOUNDS IN EXHAUST GASES

Anna Janicka, Wojciech Walkowiak, Agnieszka Sobianowska-Turek, Radosław Wróbel

Wroclaw University of Technology
Wyb. Wyspianskiego 27
50-370 Wroclaw
tel./fax. +48 71 3477918
e-mail: anna,janicka@pwr.wroc.pl

Abstract

Emission from mobile sources causes human and environment exposure to hazardous, toxic substances. Because of civilization diseases expansion it is very important to estimate a toxic influence of emitted by combustion engine substances on human health. This paper presents the results of analysis of platinum-rhodium active coating application in diesel engine on toxicity of volatile organic compounds (VOC's) in exhaust gases.. The catalyst was applied on SB.3.1 compression ignition engine valves surface. A special methodology of engine exhaust toxicity was applied: calculation of Toxic Equivalent Factor (TEF). For estimation of volatile organic compounds toxicity in the engine exhaust gases as a indicator benzene was chosen. The calculation of TEFs was base don Recommended Maximum Concentration Limits (RMCL), for one year period, according to polish Minister of Environment Directive (Dz.U.2003 nr 1 poz. 12). Toxicity Equivalent Factor was calculated for total volatile organic compounds identified in every chosen point of SB3.1 engine work and toxic. A comparison analysis of VOC's toxicity in the engine exhausts in both conditions (with and without platinum rhodium active coating on the engine valve surface) was done. The analysis results show that inner catalyst application causes significant toxicity decrease for lower engine loads for both chosen rotational speeds.

Keywords*: engine exhaust toxicity, volatile organic compounds, Toxicity Equivalent Factor*

1. Introduction

The ability of organic chemicals to cause health effects varies greatly from those that are highly toxic, to those with no known health effect. As with other pollutants, the extent and nature of the health effect will depend on many factors including level of exposure and length of time exposed. Eye and respiratory tract irritation, headaches, dizziness, visual disorders, and memory impairment are among the immediate symptoms that some people have experienced soon after exposure to some organics. Many organic compounds are known to cause cancer in animals; some are suspected of causing, or are known to cause, cancer in humans. [4]
Volatile organic compounds (VOC's) effects on human health range from odour problems to toxic or carcinogenic effects. As a consequence, more stringent legislation on VOC emission has been implemented worldwide. To comply with this legislation, the use of processes which inherently cause little or no VOC's emission is preferable [4].

A motorization is one of the most important anthropogenic source of VOC's emission. Combustion engines are responsible for benzene, formaldehyde or acriolein emission – those substances belong to VOC's group and there are known from theirs mutagenic and carcinogenic properties. Because a fact that most of volatile organic compounds are listed as being toxic not only a problem their concentration in exhausts is considered necessary to be solved but also it is very important to monitor their toxic influence on human health. The second problem is very complicated and it strongly depends of the VOC's group composition in emitted exhaust gases. Estimation of toxic influence of particular compounds in VOC's group is also very problematic because not for many substances their toxic properties are unknown. For some substances Recommended Maximum Concentration Limit (RMCL) is settled in governmental directives what constitute a base for VOC's mixture toxicity estimation by using Toxicity Equivalent Factors (TEF) [1-3].

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 Hennan-Froude engine dyno. The most characteristic points of functional engine work (engine 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 simultaneously printed paper [2].

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: colorimethry (formaldehyde marking according to directive PN-71/C-04539) and chromatography. Carbone 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 ºC), dozers (150 ºC) and detectors (250 ºC).

3. Methodology of VOC's toxicity estimation in engine exhaust

For estimation of volatile organic compounds toxicity in the engine exhausts as a indicator benzene was chosen because of its well known mutagenic and carcinogenic properties. Benzene is absorbed mainly from respiratory system and alimentary canal. Benzene and its metabolites (i.e. phenol) are able to fixation with liver proteins, bone marrow, kidney, blood, muscles and lien proteins. It cause devastation of nervous system and bone marrow (causes leukemia). Allowable benzene concentration in atmospheric air in Poland amount to 5 $\mu g/m^3$.

For the diesel engine exhaust toxicity estimation Toxicity Equivalent Factors (TEF) related to benzene was applied. Benzene was identified in the engine exhaust in every chosen point of its work. The analysis of VOC's toxicity in exhaust was based on Recommended Maximum Concentration Limits (RMCL), for one year period, according to polish Minister of Environment Directive (Dz.U.2003 nr 1 poz. 12).

TEF for total volatile organic compounds in exhaust was determinate as follow:

- Coefficient R was determinate as a benzene RMCL ratio to RMCL of particulate compound from VOC’s group (table 1),
- TEF for single VOC was calculated by multiplication its coefficient R and its concentration in exhausts,
- TEFs determinate for single VOC’s detected in exhausts was tot up. The result was TEF for total VOC’s.

For some identified in exhaust gases compounds (isovaleric aldehyde, isobutyl aldehyde and ethanol) was not possible to TEF calculated because for those substances RMCL was not determinate. Those substances was not taken into consideration in TEF for total VOC’s calculation.

Recommended Maximum Concentration Limit (RMCL), μg/m^3 , for year period, for VOC’s identified in the engine (SB3.1) exhaust and R coefficient are presented in table 1.

Tab. 1. Recommended Maximum Concentration Limit (RMCL), μg/m^3 , for year period, for VOC’s identified in the engine (SB3.1) exhaust

Compound	Chemical formula	RMCL,μg/m^3	R coefficient: $R = \frac{RMCL_{benzene}}{RMCL_x}$
Akrolein	C_3H_4O	0,9	5,556
Acetic aldehyde	C_2H_4O	2,5	2,00
MIBK (metylisobutylketone)	$C_6H_{12}O$	3,8	1,316
Formaldehyde	CH_2O	4	1,250
Benzene	$\mathbf{C_6H_6}$	**5**	**1,00**
Toluene	C_7H_8	10	0,500
Xylene	C_8H_{10}	10	0,500
Butyl alcohol	$C_4H_{10}O$	26	0,192
Acetone	C_3H_6O	30	0,167
Ethylbenzene	C_8H_{10}	38	0,132
Heptane	C_7H_{16}	1000	0,005
Hexane	C_2H_{14}	1000	0,005
Octane	C_8H_{18}	1000	0,005
Nonane	C_9H_{20}	1000	0,005
Isovaleric aldehyde	C_4H_9O	No data	---
Ethanol	C_2H_6O	No data	---
Propionate aldehyde	C_3H_6O	No data	---
Isobutyl aldehyde	C_4H_8O	No data	---

Based of quantity-quantitative analysis [2] Toxicity Equivalent Factor was calculated for total volatile organic compounds identified in every chosen point of SB3.1 engine work.
Toxicity Equivalent Factors (TEFs) for total volatile organic compounds emitted by the self-ignition engine are presented in table 2.

Tab 2. Toxicity Equivalent Factors (TEFs) for total volatile organic compounds emitted by the compression ignition engine

Engine work conditions	Engine work phase						
	1200 r.p.m.				1600 r.p.m.		
	5 Nm	10 Nm	20 Nm	30 Nm	10 Nm	20 Nm	30 Nm
	Toxicity Equivalent Factor (TEF)						
Initial conditions (engine without catalyst)	0,00605	0,00775	0,01003	0,01322	0,02434	0,01572	--
Engine with Pt/Rh catalyst	0,00125	0,00627	0,00805	0,01431	0,00546	0,03561	0,02189

A variability of Toxicity Equivalent Factor if function of engine speed and engine load for initial conditions (engine without catalyst) is presented on figure 1.

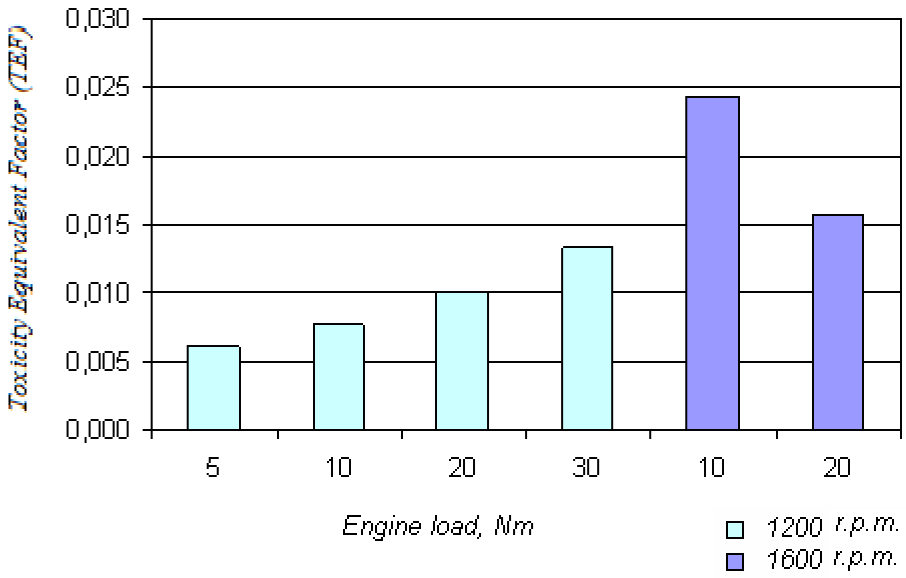

Fig.1. Volatile organic compounds toxicity emitted by SB3.1 diesel engine (initial conditions – engine without catalyst)

When engine was working with lower engine speed (1200 r.p.m.) increase of VOC's toxicity with engine load was observed – this trend was compatible with VOC's concentration and it is also correlated with formaldehyde concentration increase in exhausts [2].

When engine was working with higher engine speed (1600 r.p.m) and inverse trend was observed – the highest TEF characterized VOC's emitted when engine was working with lower load (10 Nm) and for lower load (20 Nm) 30 % TEF reduction was observed.

After platinum-rhodium inner catalyst application similar situation was noticed for engine speed 1200 r.p.m. (figure 2). When engine was working on 1600 r.p.m. engine speed level the highest value of TEF was observed for middle engine load (20 Nm). The tendency of TEF variability is very similar to formaldehyde concentration in this conditions of engine work (engine with catalyst) [2].

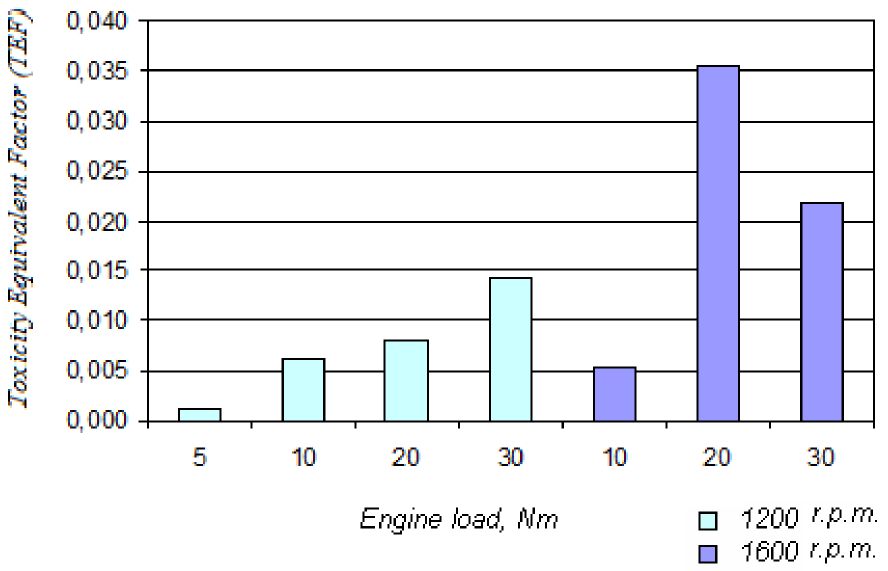

Fig.2. Volatile organic compounds toxicity emitted by SB3.1 diesel engine (initial conditions – engine without catalyst)

A comparison analysis of VOC's toxicity in the engine exhaust gases in both conditions (with and without platinum rhodium active coating on the engine valve surface) was done. The analysis results show that inner catalyst application causes significant toxicity decrease for lower engine loads for both chosen engine speeds (figure 3).

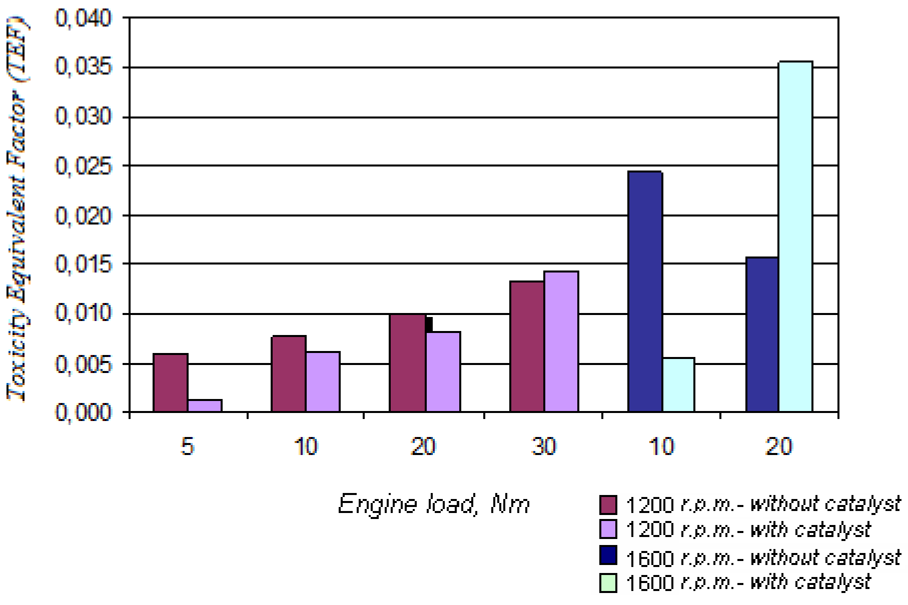

Fig.3. A comparison of VOC's toxicity emitted with SB3.1 diesel engine exhaust

When engine was working whit higher load decrease of catalyst effectiveness was observed. For the highest engine loads (for both engine speeds) catalyst application caused the aggravation of exhaust quantity in their toxicity aspect.

4. Conclusions

1. The platinum-rhodium active coating application causes significant toxicity decrease for lower engine loads, but the catalyst effectiveness was decreasing rapidly with engine load rising.
2. Engine exhausts toxicity strongly depends on exhaust composition (participation of the most toxic compounds).
3. Toxicity Equivalent Factor, because of specific calculation method, is correlated with law regulation (is based on current regulations e.g. Recommended Maximum Concentration Limit), so its value can be changeable.

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