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EXTENDED COMPOSITION OF SELF-IGNITION ENGINE COMBUSTION GAS

Car emissions contribute markedly to the global pollution of environment. As a result of incomplete combustion of hydrocarbon fuel, many toxic substances (carbon monoxide, aromatic and paraffin hydrocarbons, aldehydes, ketones, alcohols and PAHS) are discharged into the atmosphere. Tests have been conducted on true combustion gases released during the operation of a self-ignition engine in the engine test house. The measuring system was supplied with the equipment for collecting the samples that made it possible to take the exhaust gas before and after its passing through the catalyst. The chromatographic analysis of the exhaust gases emitted from a self-ignition engine allowed us to determine 23 volatile organic compounds. It was found out that with the increase in the turning moment of the engine, the concentrations of all impurities decreased. The catalyst under investigation decidedly reduced the emission of toxic compounds contained in the exhaust gas at the stabilised engine operation. With the addition of ethyl alcohol to a commercial fuel the concentration of the most toxic impurities (benzene and acrolein) increased twice.

1. INTRODUCTION

The intensive development of motorization resulted in a serious pollution of air by exhaust gases from driving motors. Threats due to motor combustion gas increase with the increase in the harmfulness of its components that are emitted directly into the atmosphere. Vehicles are driven mainly in cities, i.e. places where people live in closed areas. In such places, the conditions of natural air exchange are usually limited by dense building development. From statistical data it follows that motor traffic in our country is the source of the half of gaseous impurities emitted into the atmosphere [1].

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The impurities occurring in the exhaust gas are products of liquid fuel combustion, which in a real engine is incomplete and defective, or they may join together to make the products of the secondary reactions. In the group of numerous organic compounds, one can identify unburned aromatic and paraffin hydrocarbons, oxy-derivative compounds such as aldehydes, ketones, alcohols, and polycyclic aromatic hydrocarbons (PAHs).

Because of their carcinogenic properties polycyclic aromatic hydrocarbons are one of the most dangerous compounds. Biologically most active is benzo (a) pyrene. Also volatile organic compounds (VOCs) present a threat to environment, because they disturb natural photolytic cycle. This results in the formation of an excessive amount of ozone whose chemical activity is particularly high. As is commonly known, in the secondary photochemical reactions, aldehydes yield peroxide acetyl nitrate (PAN), one of the most irritative and harmful compounds [2], [3].

A self-ignition motor also emits the so-called particulate matter (PM). Its particulates consist of engine black, particles of sulphur and metal compounds, inorganic compounds, as well as heavier fractions of lubricating oil and fuel hydrocarbons. In self-ignition engines, carbon black is an inseparable combustion product, whose formation is conditioned by their operation principle and the way of forming the fuel–air mixture [5]. Therefore the level of the carbon black emission from these engines is much higher than that from spark ignition engines [4]–[6].

Environment pollution caused by motorization forced both the designers and vehicle users to undertake intensive actions allowing them to reduce its negative effect on natural environment and life of man.

Some preventive measures adopted so far comprise:

- a change in engine design and a change of physicochemical features of the fuel used,
- introduction of organisational solutions,
- mounting catalytic converter that neutralizes the impurities.

If we take the composition and temperature of combustion gases into account, catalytic combustion seems to be a particularly useful method of reducing toxic impurities.

In the paper, there are presented the results of the investigations carried out in order to determine the composition of combustion gas (both qualitative and quantitative) produced by the engine operating at various parameters of its load and burning different kinds of fuel.

2. EXPERIMENTAL

Actually used combustion gases were tested during the operation of a self-ignition engine in the engine test house. In the tests, the engine of the power of 80 kW and with a direct fuel injection was used. Besides other machines, also mining working machines are equipped with such a type of engine. The engine was fed with commercial diesel oil and with diesel oil enriched by an ethyl alcohol. In the engine exhaust system, a platinum–palladium catalyst was installed.

Taking pattern of the European toxicity test (according to the ECE R 49 Regulations; in Poland BN-84/1374-12), testing according to a 9-phase load cycle has been performed determined by the engine crankshaft rotational speed n (measured in turns/min), the turning moment M_0 of the engine (in Nm), and the exhaust gas temperature t_s (in centigrade):

Series I,	$n = 1600$ turns/min;	$M_0 = 40$ Nm,	$t_s = 188$ °C.
Series II,	$n = 1600$ turns/min;	$M_0 = 100$ Nm,	$t_s = 240$ °C.
Series III,	$n = 1600$ turns/min;	$M_0 = 200$ Nm,	$t_s = 352$ °C.
Series IV,	$n = 1600$ turns/min;	$M_0 = 300$ Nm,	$t_s = 469$ °C.
Series V,	$n = 900$ turns/min;	$M_0 = 0$ Nm,	$t_s = 113$ °C.
Series VI,	$n = 2300$ turns/min;	$M_0 = 270$ Nm,	$t_s = 510$ °C.
Series VII,	$n = 2300$ turns/min;	$M_0 = 150$ Nm,	$t_s = 368$ °C.
Series VIII,	$n = 2300$ turns/min;	$M_0 = 90$ Nm,	$t_s = 313$ °C.
Series IX,	$n = 2300$ turns/min;	$M_0 = 36$ Nm,	$t_s = 259$ °C.

The measuring system was supplied with such an equipment for collecting the samples that enables us to take the exhaust gas before and after its passing through the catalyst. The exhaust gas was drawn into tubes with active carbon and then extracted using carbon disulphide.

The analysis of the extracts obtained was carried out using a gas chromatograph, Hewlett Packard 5890 Series II, equipped with a flame ionisation detector, capillary column HP-5 of the length of 30 m and 0.56 mm in diameter. The analysis was made at the column temperature of 110 °C. The feeder and the detector temperature reached 150 °C.

The results obtained were processed by means of the AKORD computer program. In order to determine quantitatively the components of the exhaust gas, calibration coefficients for particular components had to be determined.

The outdrops taken to washers placed before the tubes with active carbon were analysed mainly for the content of formaldehyde by photocolorimetric method. The absorption was measured at the wavelength of 570 nm.

The effectiveness of the catalyst action was determined based of the concentrations of particular components of exhaust gases before and after their passing through the reactor.

3. RESULTS AND DISCUSSION

The chromatographic analysis of the exhaust gases emitted from a self-ignition engine made it possible to determine 23 volatile organic compounds representing four main groups:

• aldehydes (formaldehyde, acetic aldehyde, propionaldehyde, isobutyl aldehyde, butyl aldehyde, isovaleric, valeric, acrylic, oenanthic, benzoic, caprylic aldehydes),

• hydrocarbons as total concentrations of aromatic and paraffin hydrocarbons (benzene, toluene, xylene, ethylbenzene, cumene, cymene, butylbenzene, hexane, octane, nonane, decane, undecane),

• alcohols (amyl, isoamyl, hexyl, heptyl, benzyl alcohols),

• ketones (methyl isobutyl ketone).

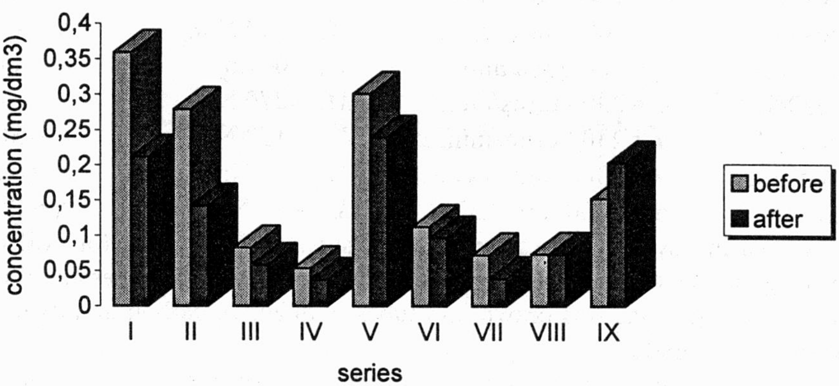

Fig. 1. Concentrations of aldehydes before and after their passing through the catalyst

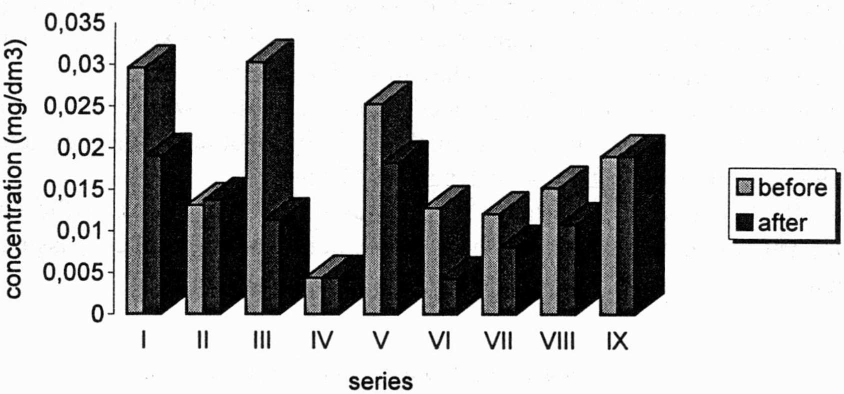

Fig. 2. Concentrations of hydrocarbons before and after their passing through the catalyst

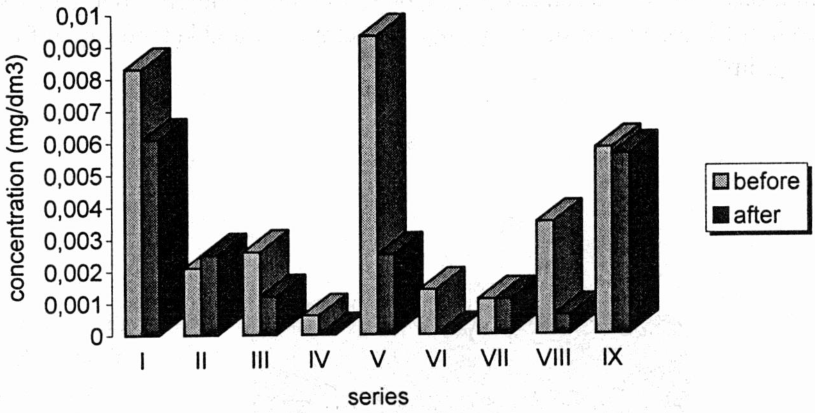

Fig. 3. Concentrations of alcohols before and after their passing through the catalyst

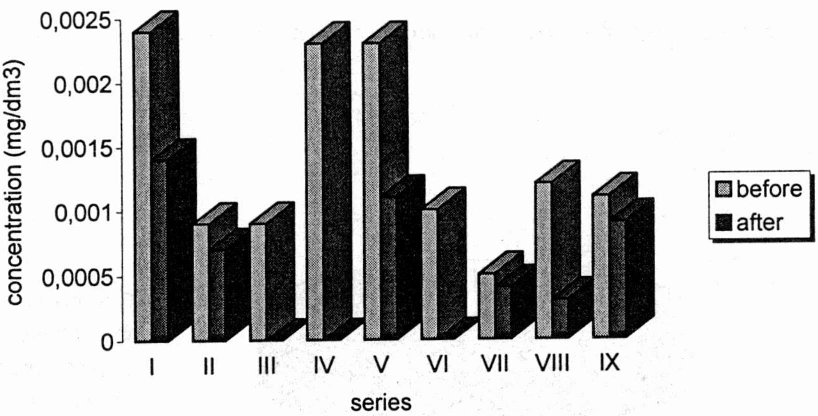

Fig. 4. Concentrations of ketones before and after their passing through the catalyst

Total concentrations of particular groups of compounds included in combustion gases formed during commercial fuel combustion, depending on engine speed and torque, are presented in figures 1–4. Together with the increase in the engine speed and torque, a temperature of the exhaust gas and its qualitative and quantitative composition changed. In volatile organic compounds contained in combustion gases, aldehydes were playing a dominant part; their concentrations ranged from 0.359 do 0.053 mg/dm^3, while the concentrations of hydrocarbons were almost ten times lower (0.03–0.0044 mg/dm^3). Still low concentrations of alcohols ranged from 0.0093 to 0.0006 mg/dm^3, but it was ketones that occurred in the lowest concentration – that of methyl isobutyl ketone varied from 0.0024 to 0.0005 mg/dm^3.

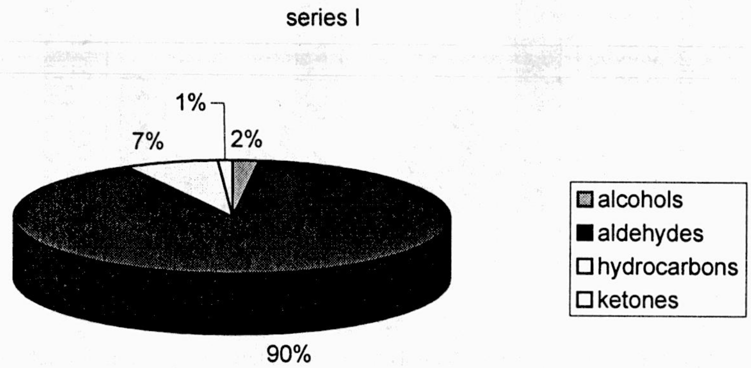

Fig. 5. Percentage share of particular groups of volatile organic compounds in series I

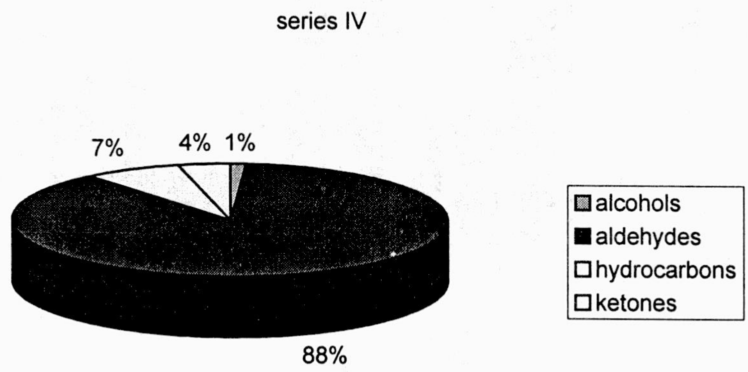

Fig. 6. Percentage share of particular groups of volatile organic compounds in series IV

Together with the increase of the torque causing the decrease of the excess air coefficient, the concentrations of aldehydes, hydrocarbons, alcohols and ketones basically decreased at both rotational speeds (1600 and 2300 turns/min). The concentration of the compounds occurring in the exhaust gases at low loads is comparable to or somewhat higher than that at a zero turning moment. For aldehydes (figure 1) these concentrations amount to 0.359 and 0.301 mg/dm^3 (phases I and V), for hydrocarbons (figure 2) – 0.0269 and 0.0253 mg/dm^3, for alcohols (figure 3) – 0.0085 and 0.0093 mg/dm^3, whereas for ketones (figure 4) – 0.0024 and 0.0023mg/dm^3. Along with the increase of the turning moment, the concentration of all impurities in the exhaust gas decreased, but no basic change in the mass composition was observed, particularly for the impurities occurring in the highest concentrations, i.e. for aldehydes and hydrocarbons (figures 5 and 6).

For the rotational speed of 1600 turns/min, both for the torque of 40 and 300 Nm, the share of hydrocarbons was not changed, whereas that of the aldehydes changed inconsiderably (from 90 to 88%). On the other hand, the per cent share of the alcohols and ketones occurring in considerably lower concentrations in the exhaust gases changed substantially. The number of alcohols decreased twice, whereas that of ketones increased four times.

In the exhaust gas, the effectiveness of the reactions of the impurities in the presence of catalyst depended on the load and the turning moment (table 1). Our investigations proved that the activity of the catalyst was the highest when ketones and alcohols were reheated. At great turning moments, when the exhaust gas temperature exceeded 400 °C, both those groups underwent a 100% transformation, whereas the reheating of hydrocarbons resulted in their 65% conversion.

Table 1

Efficiency of oxidation of particular groups of compounds [%]

Compound	Series No.								
	I	II	III	IV	V	VI	VII	VIII	IX
Aldehydes	42	49	30	31	20	15	45	–25	–27
Hydrocarbons	30	–5	62	1	28	65	33	30	12
Alcohols	26	–18	55	100	75	100	10	84	4
Ketones	44	24	100	100	50	100	20	75	18

Combustion of aldehydes was not efficient, as it approached maximally 50% and their concentration even increased after their passing through the catalyst (for small turning moments and a higher rotational speed of 2300 turns/min).

This may prove that under these conditions, the hydrocarbons burned in the presence of catalyst give rise to intermediate products, i.e. aldehydes. The lowest effectiveness of the catalyst action was observed for idle running (at zero torque) and the lowest loads of the engine when the exhaust gas temperature is the lowest. In the tests carried out for idle running, after a longer engine operation, a better effectiveness of the catalyst action was observed at low engine loads.

Emission of carbon black sometimes resulted in catalyst deactivation (series II). However, the catalyst tested was capable of being self-regenerated.

The exhaust gas composition of both fuels tested, i.e. commercial and that with an alcohol addition, under selected conditions of the engine operation was presented in table 2. In this table, the total concentrations of the compounds investigated and the most toxic impurities occurring in the exhaust gas such as acrolein and benzene are specified.

Table 2

Concentrations of the compounds formed during the combustion of commercial fuel and ethanol-added fuel

Measurements	Compound	Fuel concentration [mg/dm^3]	
		Commercial	With methanol addition
series IV	aldehydes	0.0534	0.0451
t_s = 467 °C	ketones	0.0023	0.0010
n = 1600 turns/min	alcohols	0.0006	0.0042
M_0 = 300 Nm	hydrocarbons	0.0044	0.0047
	formaldehyde	0.0240	0.0108
	acrolein	0.0018	0.0038
	benzene	0.0028	0.0060
	propionaldehyde	0.00168	0
series V	aldehydes	0.3007	0.1448
t_s = 105 °C	ketones	0.0023	0.0026
n = 900 turns/min,	alcohols	0.0093	0.0065
M_0 = 0 Nm	hydrocarbons	0.0253	0.0301
	formaldehyde	0.0078	0.0060
	acrolein	0.0027	0.0054
	benzene	0.0062	0.0078
	propionaldehyde	0.1394	0
series VI	aldehydes	0.1124	0.0864
t_s = 507 °C	ketones	0.0010	0.0022
n = 2300 turns/min	alcohols	0.0014	0.0083
M_0 = 270 Nm	hydrocarbons	0.0128	0.0248
	formaldehyde	0.0625	0.0296
	acrolein	0.0030	0.0065
	benzene	0.0018	0.0041
	propionaldehyde	0.0211	0

The alcohol added to a commercial fuel changed in a selective way the concentration of the impurities in the exhaust gases. The concentration of aldehydes that is the highest at the highest turning moment has practically inconsiderably changed at both rotational speeds tested. Only for idle running it is reduced twice.

At the rotational speed n = 1600 turns/min no change in hydrocarbon concentrations was observed, whereas at a higher rotational speed this concentration increased twice. The concentration of alcohols doubles, which seems natural. Analysing the concentration of the most toxic impurities a double increase in acrolein and benzene concentrations was found out.

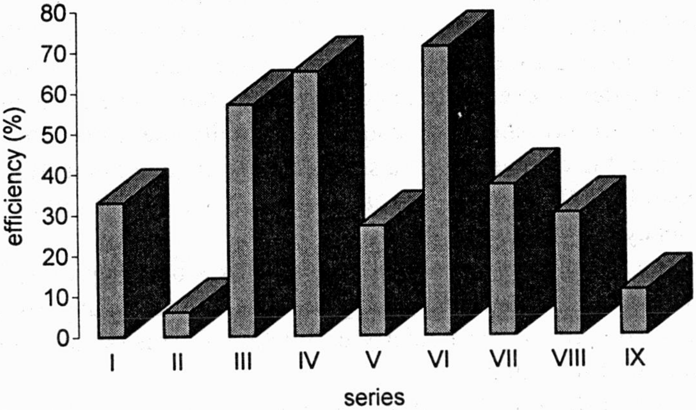

Fig. 7. Efficiency of catalyst in the reheated exhaust components of commercial fuel

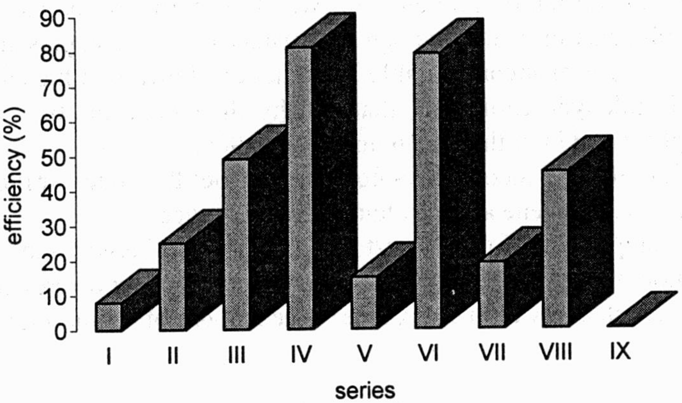

Fig. 8. Efficiency of catalyst in the reheated exhaust components of commercial fuel with ethanol addition

The catalyst effectiveness being improved due to reheating of the total amount of impurities at n = 1600 and 2300 turns/min as well as M_0 = 300 and 270 Nm for commercial fuel ranged from 65 to 70%, whereas that for the fuel with the alcohol addition – from 78 to 80%. At the idle running the effectiveness is 10% better for commercial fuel (figures 7 and 8).

4. SUMMING-UP

In order to eliminate or at least to reduce the emission of volatile organic compounds contained in exhaust gases from self-ignition engines, it is necessary to guarantee good technological state of an engine, correct vehicle operation, and an efficient catalyst.

It was found out that with the increase in the turning moment of the engine, the concentrations of all impurities decreased (the concentration of hydrocarbons – six times, that of aldehydes – seven times, and that of alcohols – even fifteen times).

The catalyst under investigation reduces essentially the emission of toxic compounds contained in the exhaust gas at a stabilised engine operation. With the increase in the engine load the efficiency of the catalyst increases. At idle running and at low loads this efficiency is considerably poorer.

Carbon black, a component of exhaust gases, causes blocking of active centres of the catalyst, which obstructs the reheating process, and subsequently increases the concentrations of compounds, particularly of aldehydes. This occurs sporadically due to self-regeneration of the catalyst.

Testing the combustion of the mixture of organic compounds should be based on the analysis of their total concentration. It seems reasonable to test the combustion gas composition in such a way as to control the concentrations of the most toxic compounds. In the combustion process in the engine, the hydrocarbons included in the fuel undergo a transformation into alcohols which, in turn, are oxidised to aldehydes and ketones. This reaction is fast enough to consider the percentage share of the alcohols in the exhaust gas as inconsiderable. The fuel combustion in the engine is mainly associated with aldehyde formation, that is why their concentration in combustion gases is the highest and in both cases it approaches 90%.

With addition of ethyl alcohol to a commercial fuel the concentration of the most toxic impurities, i.e., benzene and acrolein, increases twice.

Testing the composition of the exhaust gas should not be based on the analysis of the total concentration of organic compounds. It seems reasonable to determine the composition of this gas in such a way as to control the concentrations of the most toxic impurities.

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ROZSZERZONY SKŁAD SPALIN SILNIKA O ZAPŁONIE SAMOCZYNNYM

W globalnej emisji zanieczyszczeń środowiska znaczny udział ma motoryzacja. W wyniku niepełnego spalania paliw węglowodorowych do środowiska dostają się takie substancje toksyczne jak: CO, węglowodory aromatyczne i parafinowe, aldehydy, ketony i alkohole oraz WWA. Badania przeprowadzono na rzeczywistych gazach spalinowych podczas pracy silnika o zapłonie samoczynnym na stanowisku hamownianym. Układ pomiarowy wyposażono w aparaturę do poboru prób, co umożliwia pobór gazów przed i za katalizatorem. Metodą analizy chromatograficznej oznaczono 23 lotne związki organiczne. Stwierdzono, że wraz ze zwiększeniem momentu obrotowego silnika stężenia wszystkich zanieczyszczeń malały. Badany katalizator w istotny sposób zmniejsza emisję toksycznych związków zawartych w gazach spalinowych przy ustabilizowanej pracy silnika. Dodatek alkoholu etylowego do paliwa powoduje dwukrotny wzrost stężeń najbardziej toksycznych zanieczyszczeń: benzenu i akroleiny.