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Internal Combustion Engine Response to Presence of Combustion Inhibitors in Ambient Air

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ABSTRACT

Many motor vehicles (fire-fighting cars and trucks, helicopters, airplanes etc.) are used for conflagration extinguishing purposes. It is clear that their engines aspirate air containing combustion inhibitors, which are used for flame suppression, but until now there is no available information about the influence of this fact on engine performance. This paper presents results of an experimental study on the influence of combustion inhibitors, such as Halon 1301 (CF₃Br) and CO₂, contained in the ambient air, on the performance of compression ignition (CI) and spark ignition (SI) engines. Substantial differences in the response of CI and SI engines to the inhibitor presence in the aspirated air are revealed. Starting from relatively small concentrations of CF₃Br, an increase of the CI engine speed and a simultaneous decrease of the brake specific fuel consumption are observed. The speed rise may attain up to 80% of its initial value. Dramatic deterioration, approximately by a factor of 3, in the efficiency of the SI engine's catalytic converter (CC) is observed after a short-time exposure of the SI engine to the ambient air containing Halon 1301. Chromatographic analysis of exhaust gases during an exposure of the engines to CF₃Br inhibitor shows the presence of harmful substances that are highly corrosive, and dangerous for human health.

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INTRODUCTION

Modern conflagration extinguishing technologies require the use of various motorized vehicles, such as fire-fighting cars, trucks, helicopters, airplanes etc. At the fire area their engines aspirate air containing combustion inhibitors, products of their thermal decomposition and chemical reactions. These species, aimed at fire quenching, can affect the engine combustion process and consequently its performance.

Peculiarities of using different combustion inhibitors, including their optimal concentrations, chemical processes, transitional and final decomposition products are discussed in detail in the scientific literature [1,2,3,4,5,6,7,8,9,10]. All these works refer to typical fire conditions: atmospheric pressure and ambient oxygen concentrations, flame propagation speed and non-premixed air-fuel mixtures [7]. Contrary to this, there is no available literature on the influence of combustion inhibitors on the performance of internal combustion engines (ICE), where in-cylinder fuel combustion conditions differ radically from those typical for fire expanding. The combustion process in ICE is featured by substantially higher pressures (up to 150 bar) and

temperatures (up to 2500 $^{\circ}$ C), turbulent flame, and sometimes by premixed air-fuel mixture with a strongly limited oxygen concentration.

The most common combustion inhibitors may be divided to two main groups depending on the principle of their operation. Inhibitors of the first group, which may be called "passive", decrease oxygen concentration in the flame zone simply by replacing part of the ambient air. This leads to a decrease of the combustion velocity or complete flame quenching. CO₂ is the typical and most well-known combustion inhibitor of this group. Its relatively high specific heat contributes additionally to a flame quenching process. Water use for flame suppression was not considered in this work. Inhibitors of the second group, which may be called "active", can cut-off combustion chain reactions of hydrocarbon fuels [1, 4, 5], thus preventing the flame propagation. The typical inhibitors of this group are the Halons, such as Halon 1301 (CF₃Br), Halon 1211, (CF₂ClBr), and others. The latter is less accepted because one of the products of its high temperature decomposition in air is the highly toxic gas phosgene COCl₂ [1, 6]. As the Halons

are considered to be ozone-depleting fire extinguishers, their use at present is restricted.

It was found in previous studies carried out at atmospheric conditions [$\underline{1}$, $\underline{4}$] that the air surrounding a hydrocarbon fuel flame inhibited by Halon 1301 contains the toxic products of its thermal destruction and chemical reactions: HF, HBr, CF3H, and CF2O, in addition to the unreacted combustion inhibitor CF3Br. These species are harmful to human health and may be expected to be present in exhaust gases of ICE operating in a fire area. Additionally, some of these materials are highly corrosive (e.g. HF, HBr [$\underline{11}$]) and may damage the engine internal surfaces.

The response of the two different ICE types, SI and CI, to the presence of combustion inhibitors in aspirated air can be different, because of fundamental differences in their working process, expressed in fuel/air mixture quality, type of combustion, etc. For example, the absolute majority of SI engines operate at all speed and load regimes under air/fuel ratio in the vicinity of stoichiometric (λ =1) and premixed combustion. In contrast, CI engines always operate with an excess of oxygen and mixing controlled combustion. Lambda value in a diesel engine is usually not lower than 1.2-1.3 under full load regimes and well exceeds 5 at idle and low loads. Taking these differences into account, studying the sensitivity of both engine types to the presence of combustion inhibitors in the aspirated air seems to be essential.

The goal of this work was an assessment of ICE performance in response to different concentrations of combustion inhibitors in the aspirated air. The influence of two typical representatives of passive, CO₂, and active, Halon 1301, combustion inhibitors was studied. For both CI and SI engines operated with the aspirated air containing Halon 1301 a chromatographic analysis of exhaust gases was performed to determine possible presence of harmful substances dangerous for human health and engine internal surfaces. An effect of combustion inhibitors on efficiency of catalytic converter was discovered and assessed as well.

METHODOLOGY

The study was carried out at the laboratory experimental rigs based on the engine dynamometer test benches. Main features of the engines participated in the experiments are presented in Table 1.

The engines were tested at steady-state regimes and loaded by the eddy current dynamometers: Hoffman IRD (SI engine) and Schenck E90 (CI engine). The SI engine was tested with both types of combustion inhibitors over two load characteristics, and four load regimes at each engine speed. The CI engine was tested over two load characteristics and four load regimes at each engine speed with Halon 1301. CO_2 influence on the performance of CI engine was studied over one load characteristic. The operation regimes of both engines, where measurements were carried out, are presented in Table 2.

Table 1. Main features of tested engines

Engine type	SI	CI
Fuel type	Gasoline 95	Diesel fuel
Fuel injection and	Single point	Indirect injection,
mixing type	injection	Divided chamber
Number of cylinders	4	4
Displacement, cc	1400	1900
Bore x Stroke, mm	75.8 x 77	80 x 93
Compression ratio	9.5	18.3
Rated power, kW at	59.6 @ 6000	59 @ 4000
speed, rpm		
Max. torque, Nm at	109 @ 3500	160 @ 2000
speed, rpm		

Table 2.	Operation	regimes	of tested	engines
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Engine type	SI		CI		
Inhibitor	CO ₂ and	d CF ₃ Br	CF ₃	Br	CO ₂
Speed, rpm	2500	3500	1800	2200	2000
Torque, Nm	30	30	40	40	40
	45	45	55	55	60
	60	60	70	70	80
	75	75	85	85	86.5

The laboratory experimental rigs were instrumented with equipment for metered supply of combustion inhibitors into the engine intake manifold and by the data acquisition system (see Fig.1).



Figure 1. Scheme of the laboratory engine test rig equipped with facilities for combustion inhibitors metered supply and exhaust gases sampling

The engine 1 loaded by the dynamometer 2 was fuelled from tank 3 through the fuel flow meter 4, BROOKS LS 4150 (Japan). In the case of the CI engine, the fuel system was additionally equipped by the return line 14 with a fuel cooler and a remote-control three-way valve. The latter was connecting the return line with the feeding line at the time of the fuel consumption measurement. The engine was aspirating air through the air filter 5 and the air flow meter of Meriam 50MR2-2 type. Each inhibitor was kept in a pressurized cylinder 8 with a stopcock 9. The Halon 1301 cylinder was the handheld extinguisher and contained 3 kg of the inhibitor under the pressure of approximately 10 bar. The CO₂ cylinder contained 2 kg of inhibitor under the pressure of approximately 50 bar. This pressure required using a pressure reducer 17 in the experiments with CO₂. Cylinders with the inhibitors were installed on the GF-12K digital balance 7 with an analog output. Metering of the inhibitor supply was carried out by a heated needle valve 12. The heating was realized by a 300°C hot air blower 11 and was needed for preventing the inhibitor freezing, as a result of expansion, inside the valve. A rotameter 13 was used for the visual control of the inhibitor flow rate stability. The inhibitor cylinder 8 and the valve 12 were connected by a flexible hose 10.

The inhibitor mass supply was assessed gravimetrically as a change in the balance readings per known time period. Inhibitor concentration was calculated as a ratio between its mass supply rate and the engine intake air mass flow rate. All the measured data: engine speed and torque values; exhaust gas, lubricant and coolant temperatures; intake air, fuel and inhibitor flow rates were logged with a 1Hz frequency by data acquisition system 15 and computer 16. Data on the measurements accuracy is shown in <u>Table 3</u>.

Parameter	Device	Uncertainty
Engine speed	Schenk/Hoffman	±9 rpm
	dynamometer	
Engine torque	Schenk/Hoffman	±1 Nm
	dynamometer	
Temperatures	K-type thermocouples	$\pm 1.5^{\circ}C$
Fuel flow rate	Brooks LS4150	±1%
Intake air flow rate	Meriam 50MR2-2	±0.011
		m ³ /min
Inhibitor supply	GF-12K digital balance	±0.6 g

 Table 3. Measurements accuracy

Catalytic converter efficiency (for the SI engine only) was assessed before and after the experiments with the Halon 1301 combustion inhibitor by using the following equation:

$$E_{i} = \frac{(C_{i}^{before} - C_{i}^{after})}{C_{i}^{before}} \cdot 100\%$$

Where: E_i - conversion efficiency for the pollutant *i*; C_i^{before} - concentration of pollutant *i* in the exhaust gases before the entrance of exhaust gas to the CC; C_i^{after} - concentration of pollutant *i* at the exit of exhaust gas from the CC. Measurements of CO and total HC concentrations in the engine exhaust gases were carried out by the Bosch BEA type non-dispersive infrared gas analyzer.

The engine response to the inhibitor presence in the aspirated air was studied with a step-by-step increase of the inhibitor supply at each engine operation regime. All the measurements and exhaust gases sampling were carried out under steady-state conditions, after stabilization of the engine thermal regime.

Exhaust gas sampling for the chromatographic analysis was carried out at the following operation regimes: the SI engine - 50 Nm @ 3500 rpm and one concentration value of the combustion inhibitor CF_3Br ; the CI engine - 40 Nm (a) 2200 rpm and three different concentration values of Halon 1301. The sampling for inorganic acids analysis was carried out directly from the engine exhaust pipe using the SKC 224-PCX4 AIRCHEK sampler pump and the 226-10-03 glass bulbs filled with silica gel (positions 18 and 19 in Fig.1). The sampling for the analysis of organic species was carried out at the same point of the exhaust pipe by using the same sampler pump and the SKC 226-01 glass bulbs. The analysis of inorganic acids was fulfilled by an ion chromatography according to the NIOSH-7903 method. The analysis of organic species was fulfilled by the GC-MS gas chromatograph.

RESULTS AND DISCUSSION

SI Engine, Halon 1301

Typical example of SI engine response to the presence of different Halon 1301concentrations in the aspirated air is presented in <u>Fig.2</u>.



Figure 2. Example of SI engine response to the presence of Halon 1301 in aspirated air. Initial regime 60Nm @ 3500rpm

As shown in <u>Fig.2</u>, the engine speed is moderately decreased starting from the inhibitor mass concentration of approximately 1.5%. Under the concentration of approximately 7% the engine speed dropped by nearly 30%. Since the dynamometer was automatically supporting the engine torque at a practically constant level, this decrease of the speed resulted in the same reduction of the engine power. It should be noted that under this decrease of the engine speed the intake air mass flow rate dropped only by 13%. This may be explained by a rise of the engine's volumetric

efficiency with a decrease of its speed. The latter is a result of the charge cooling by the inhibitor and the reduction of throttling losses due to the speed decrease. This was accompanied by some increase of the cycle fuel consumption as a reaction of the engine closed-loop control system to the increase in cycle air flow. A further rise of the inhibitor concentration caused a progressive drop of the engine speed.

<u>Fig.3</u> presents the mass concentrations of Halon 1301 in the aspirated air at different operation regimes of the SI engine that caused a 10% power reduction. The values of these concentrations may be assessed as 4.0-5.8% under 2500 rpm and 1-3% under 3500 rpm.



Figure 3. Mass concentrations of Halon 1301 in aspirated air of SI engine that caused a 10% power reduction

SI Engine, CO₂

Typical example of the SI engine response to the presence of CO_2 in the aspirated air is presented in <u>Fig.4</u>.



Figure 4. Example of SI engine response to the presence of CO_2 in aspirated air. Initial regime 60Nm @3500rpm

This response was found to be very similar to the one for Halon 1301. The engine speed began decreasing gradually after CO₂ mass concentration achieved the value of 3%. Under CO₂ concentration of approximately 11%, the engine speed and power dropped by nearly 30%. This was accompanied by a decrease in intake air flow by approximately 35%. A further rise of CO₂ mass concentration was followed by a quick drop of the engine speed and power.

<u>Fig.5</u> presents volume concentrations of CO_2 in aspirated air at different operation regimes of the SI engine caused a

10% decrease of its power. They may be assessed as 3.6 - 7% under 2500 rpm and 4 - 6% under 3500 rpm.



Figure 5. Mass concentrations of CO₂ in aspirated air of SI engine that caused a 10% power reduction

CI Engine, Halon 1301

Halon 1301 presence in the aspirated air of the CI engine led to an unexpected effect - substantial increase (by a factor of up to 1.8) of the engine speed, as shown in Fig.6. Since the engine load was automatically kept constant, this rise of the engine speed resulted in a corresponding increase of its power. This phenomenon was accompanied by a light decrease of the cycle fuel consumption. As a rule, the engine speed reached its maximal value under certain concentration of the inhibitor, different for each of the tested load and speed regimes.



Figure 6. Example of CI engine response to the presence of Halon 1301 in aspirated air. Initial regime 40Nm @ 2200rpm

<u>Fig.7</u> shows Halon 1301 volume concentration values in the aspirated air that led to the maximal rise of the engine speed under different operation regimes. The maximal speed values that were reached at these regimes are also shown in <u>Fig.7</u>. After the engine speed reached its maximal value, a further increase in the inhibitor concentration resulted in a gradual reduction of the speed.



Figure 7. Halon 1301concentration values in the aspirated air (a) that caused maximal rise of CI engine speed (b)

The above-described phenomenon that was unforeseen during the study planning was not investigated in-depth in the framework of this work. Chemical and physical mechanisms of the CF₃Br interaction with oxygen and diesel fuel under high pressures and temperatures typical for the CI engine working process still remain unclear. However, it is known from the study of Burgess et al. [10], who studied kinetics of fluorine inhibited hydrocarbon flames at atmospheric conditions, that all of the fluorinated hydrocarbons are eventually decomposed and then burned (forming CO₂, H₂O, and HF). This liberates heat and increases flame temperatures (which of course speeds flame chemistry). On the other hand, the agents are large molecules with many atoms. Consequently, their high heat capacities lead to a decrease in the flame temperature prior to complete combustion (which of course slows flame chemistry). Burgess et al. [10] mentioned that the competition between these two factors is strongly dependent upon conditions, most important of which are the mechanics of the fuel and oxidizer mixing. Thus, it can be supposed that under conditions typical for diesel process (mixing controlled combustion with the excess air at high pressures and temperatures) the former mechanism prevails until the critical inhibitor concentration is reached. In-depth study of the observed phenomenon in further research can be an interesting continuation of this work.

CI Engine, CO₂

Contrary to the SI engine response to the presence of CO_2 in the aspirated air, the CI engine speed and power remained practically constant up to relatively high concentrations of the inhibitor, as shown in <u>Fig.8</u>. This took place despite the fact that the intake air flow rate monotonously decreased with a rise of the CO_2 concentration. It is clear that the reason for this fact was a partial replacement of the intake air by the inhibitor. A decrease of the air flow rate did not result in a sensible deterioration of the engine performance (power, speed, fuel consumption, etc.) until a certain minimal value of the excess air ratio was achieved. A further increase in the CO_2 concentration of the engine speed.



Figure 8. Example of CI engine response to the presence of CO₂ in aspirated air. Initial regime 40Nm@2000rpm

The CO₂ concentration values that caused a 10% decrease in the CI engine power at different operation regimes are presented in <u>Fig.9</u>. These values were higher by about an order of magnitude than those measured for the SI engine. They decreased with the load rise when the excess air value dropped down.



Figure 9. Mass concentrations of CO₂ in aspirated air of CI engine that caused a 10% power reduction. Engine speed 2000 rpm

Catalytic Converter Efficiency

An influence of Halon 1301 presence in the intake air on the CC conversion efficiency was evaluated. This assessment was performed by a comparison of the conversion efficiency values before and after the experiments described above with the SI engine. CO and total HC concentrations in the exhaust gases were measured upstream and downstream of the CC and its efficiency under all tested operation modes was

calculated. Fig. 10 shows the mean value of the obtained results. As can be seen, a dramatic deterioration of the CC conversion efficiency was found after a short time (less than 1 hour in total) CC exposure to exhaust gases containing products of Halon 1301 decomposition. One of the possible reasons of such negative influence on the CC may be a well-documented high reactivity of the fluoric acid with silicon and aluminum oxides [11], which are the vital constituents of a CC's washcoat. The washcoat destruction will inevitably lead to a dramatic reduction in the CC conversion efficiency, because of the sharp decrease in the contact surface between the exhaust gas and the catalytic material.



Figure 10. Conversion efficiency of CC before and after SI engine exposure to Halon 1301

Exhaust Gases Analysis

The presence of Halon 1301 in the aspirated air caused white coloration of the exhaust gases for both SI and CI engines. Based on this visual observation and available data on toxic gases production during an inhibition of hydrocarbon fires by CF₃Br [4], it was decided to perform a chromatographic analysis of the exhaust gas composition. Content of inorganic acids in the exhaust gases of a CI engine was measured under various concentrations of Halon 1301 in the aspirated air, as shown in Fig.11. The measurements have been performed at the operation regime of 40 Nm and 2200 rpm. The presence of HF and HBr in the exhaust gases is a result of CF₃Br-to-hydrocarbon fuel reactions in the engine cylinders. As can be seen, the concentration of the hydrofluoric acid increased substantially, by a factor of 40, when the Halon 1301 mass concentration in the aspirated air was increased only 8 times. With this, the concentration of the hydrobromic acid increased from 5 ppm to only 15 ppm. An unexpected presence of the hydrochloric acid (HCl) in the exhaust gases was revealed. This fact was observed also in [4] and may be explained by chlorine impurities of Halon 1301. As noted above, chlorine presence in the inhibitor may result in phosgene creation under some conditions and increases corrosivity of the combustion products.



Figure 11. Mass concentrations of inorganic acids in the exhaust gases of CI engine, 40 Nm @ 2200rpm

Concentration values of Halon 1301-related organic and inorganic substances that were found in the exhaust gases of CI and SI engines are shown in <u>Table 4</u>. The engine operation regimes and the inhibitor mass concentration in the aspirated air were: for the CI engine - 40 Nm at 2200 rpm and 7.9%; for the SI engine - 50 Nm at 3500 rpm and 2.5%, respectively.

Substance	Formula	CI engine	SI engine
Bromotrifluoromethane	CF ₃ Br	110.6	4.0
Bromoform	CHBr ₃	0.47	0.31
Dibromomethane	$C_2H_2Br_2$	0.42	1.70
1,2-Dibromoethane	$(CH_2Br)_2$	0.50	0.14
1,2-Dibromopropane	C ₃ H ₆ Br ₂	0.33	-
2,2-Dibromopropane	C ₃ H ₆ Br ₂	0.36	-
1,2,3-Tribromopropane	$C_3H_5Br_3$	0.14	-
Tribromoethane	$C_2H_3Br_3$	-	0.13
Bromobenzene	C ₆ H ₅ Br	-	1.96
Hydrobromic acid	HBr	7.96	25.7
Hydrofluoric acid	HF	42.8	13.8
Benzene	C ₆ H ₆	1.29	7.15
Sulfur	S	37.8	1.38
Nitric acid	HNO ₃	3.93	-

Table 4. Results of exhaust gases analysis (mass ppm)

This table presents also concentrations of benzene, sulfur, and nitric acid, which are not the inhibitor-related substances, but were found in distinct quantities. As can be seen, the main Halon 1301-related component of the CI engine exhaust gases was CF₃Br, i.e. unreacted Halon 1301. Marked concentrations of HF and HBr in the exhaust gases were found too. The latter species are the Halon 1301-related components that were found in the most significant quantities in exhaust gases of the SI engine. HF and HBr acids are well known as highly corrosive materials [11]. Therefore, their presence in the engine exhaust gas can damage the engine inner surfaces. At the same time, concentrations of the unreacted inhibitor in exhaust gases of the CI engine were found to be the most significant and higher by a factor of 25 compared with the SI engine. Other Halon-related species were presented in the exhaust gases in negligible quantities,

mainly not exceeding 1 ppm. However, it should be noted that all of them are carcinogenic, as well as eyes and respiratory tracts irritating substances, i.e. harmful to human health.

Difference in concentration levels of benzene, sulfur, and nitric acid reflected peculiarities of the CI and SI engine fuels and working process. Oxygen excess relevant for a CI engine provoked formation of HNO₃. Lack of free oxygen in the SI engine led to higher values of benzene in the exhaust gases. Differences in sulfur concentrations evidently corresponded to those in the diesel fuel and gasoline that were used in the experiments.

SUMMARY/CONCLUSIONS

The response of SI and CI engines to the presence of combustion inhibitors in the aspirated air was studied, by examining the effect of two types of inhibitors. One type suppresses the flame by decreasing oxygen concentration in the surrounding air (the example used was CO_2), and the other quenches the flame by cutting-off chemical chain reactions of combustion (Halon 1301 was used as an example).

The response of the SI engine to the presence of both types of combustion inhibitors in aspirated air was similar. The engine speed began decreasing gradually after Halon 1301 or CO₂ mass concentration achieved the value of 1.5 or 3%, respectively. Mass concentrations of combustion inhibitors in the aspirated air that caused a 10% decrease of the SI engine power were found to be 1.0 - 5.8% for Halon 1301 and -3.6 - 7% for CO2. The SI engine was more sensitive to the presence of Halon 1301 than of CO₂.

In contrast, the CI engine was found to be insensitive to CO₂ presence in the aspirated air up to relatively high concentrations of the inhibitor. The CO₂ concentrations that caused a 10% decrease of the CI engine power were higher by approximately an order of magnitude than those for the SI engine.

A substantial increase (by a factor of up to 1.8) in the engine speed and power was unexpectedly observed in the case of Halon 1301 presence in the aspirated air. This phenomenon took place in spite of the light decrease in the cycle diesel fuel consumption. The engine speed/power reached their maximal values under different inhibitor concentrations for each operation regime. After the engine speed reached its maximal value, a further increase of the inhibitor concentration resulted in rapid speed decrease. A future, in-depth study of this phenomenon may be an interesting continuation of this work. For example, a chemical kinetics simulation can provide insights into combustion aspects of this problem.

Dramatic deterioration of the CC conversion efficiency by a factor of 2.4-3 was found after a short time of the SI engine operation (less than 1 hour in total) with Halon 1301 presence in the aspirated air. It is clear that this fact may have longterm implications on the level of pollutant emissions by vehicles that were once exposed to Halon 1301 during a fire extinguishing event.

The presence of Halon 1301 in aspirated air caused both SI and CI engines to exhaust gases with a white coloration. Chromatographic analysis revealed that the main Halonrelated substances that were found in the exhaust gas of both SI and CI engines were unreacted Halon 1301, hydrofluoric acid, HF, and hydrobromic acid, HBr. HF and HBr are well known as highly corrosive materials. Therefore, their formation inside the engine can damage its inner surfaces. Other Halon 1301-related substances were present in negligible concentrations, not exceeding 1 ppm. However, all of them are harmful to human health: carcinogenic, and eyesand respiratory tract irritating substances.

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DEFINITIONS/ABBREVIATIONS

- **CC** Catalytic Converter
- CI Compression ignition
- ICE Internal combustion engine
- RON Research octane number
- SI Spark ignition