Article

Evaluation of the Use of Hydrogen Peroxide in Diesel Engine Fuels

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Evaluation of the Use of Hydrogen Peroxide in Diesel Engine Fuels

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Abstract

The article discusses issues related to the possibility of using 10% hydrogen peroxide in ZS engine fuel to reduce exhaust emissions. The additive proposed by the authors of the article is a 12% hydrogen peroxide solution. The article presents the results of engine and analytical tests carried out by the authors. The article mainly concerns the emission of toxic substances into the atmosphere in the case of an engine fuelled with standard and modified fuel. Laboratory tests showed that the cetane number increased by two units for the modified fuel. The results of engine tests showed that the fuel additive reduces the concentration of nitrogen oxides and hydrocarbons, whilst the soot content increased slightly.

Keywords: diesel engine; hydrogen peroxide; fuel combustion; vapours; emissions

1. Introduction

Current trends in the automotive industry focus on reducing emissions of greenhouse gases and toxic substances into the atmosphere. Modifying fossil fuels is a method of improving the emission performance of vehicles so that exhaust gases comply with current environmental standards. The role of fuel additives is to optimise combustion processes within the cylinder combustion chamber. The combustion of the fuel mixture and the release of heat in diesel engines trigger physical and chemical phenomena that significantly determine engine performance. Combustion phenomena that affect the thermal efficiency of the engine primarily include the efficiency of converting the fuel's chemical energy, the thermodynamic efficiency of its utilisation, and the intensity of the dynamic load exerted on the connecting rod and piston assembly. These have posed a problem throughout the history of diesel engine development. Chemical phenomena mainly concern the composition of the exhaust gases, in particular the content of smoke and toxic substances. Currently, due to environmental protection requirements, these are the main design requirements for internal combustion engines. The conditions under which combustion takes place should, above all, ensure the maximum possible release of the fuel's chemical energy (complete and total combustion), optimal mixing of air with fuel, and utilisation of the oxidiser, whilst maintaining minimal exhaust emissions. A thermodynamic analysis of the engine cycle indicates that the efficiency of heat release in a given engine is strongly dependent on the timing of the combustion process relative to the crankshaft angle. From this perspective, the optimal solution would be to burn the entire fuel charge at a constant combustion chamber volume when the piston is at top dead centre. However, in this case, the rate of heat release during the ‘ ’ phase would become excessively high, causing shock loads on the crankshaft mechanism and acoustic symptoms in the form of excessive noise. These undesirable phenomena make it necessary to spread the heat release process over a certain period of crankshaft rotation near the piston's top dead centre. The requirements for complete heat release and its efficient

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conversion into useful work, combined with low dynamic loads on the crankshaft mechanism and minimised combustion noise, are inherently contradictory. Consequently, any engineering solution aimed at optimising these parameters represents a compromise. This compromise is further constrained by the composition of the exhaust gases, which must comply with current emissions regulations. Experience shows that it is extremely difficult to achieve satisfactory results in a given engine in terms of crankshaft loads, engine noise, exhaust gas composition and fuel economy, and an optimal compromise is usually only possible with a fairly strictly defined heat release curve. One of the main challenges associated with diesel engines is the precise control and optimisation of the combustion process, so that the resulting thermophysical and chemical phenomena meet the diverse and often conflicting requirements for performance, fuel economy, durability and emissions across the entire operating range. The combustion process in a diesel engine is highly complex, as its initiation depends on achieving the conditions for fuel self-ignition. The combustion process itself also depends on numerous design factors and fuel properties, including, in particular, the self-ignition delay. One of the main strategies for reducing exhaust emissions is the implementation of catalytic exhaust after-treatment systems. In motor vehicles, catalysts are primarily integrated into the exhaust system, where they neutralise toxic compounds, including nitrogen oxides (NO_x), hydrocarbons (HC), carbon monoxide (CO) and particulate matter (PM). Conventional catalytic reactors do not directly influence the combustion process; their role is limited to purifying the exhaust gases after combustion [3]. In contrast, liquid-phase catalysts are designed to actively support combustion, inhibit the formation of toxic compounds during reactions and facilitate their in situ neutralisation. Furthermore, such catalysts inhibit the proliferation of microorganisms that degrade hydrocarbons in the fuel, which contribute to fuel ageing. Literature reports indicate that catalysts can also be used directly in the combustion chamber of compression-ignition (CI) engines. For example, in [4], zinc- and vanadium-based catalysts were used in a single-cylinder, four-stroke diesel engine. Experimental results showed a reduction in NO_x and HC emissions of approximately 70%, CO by 60% and CO_2 by 50%, confirming the effectiveness of catalytic intervention within the cylinder. Study [5] presents the results of measurements of the performance characteristics of an engine fuelled by a biofuel derived from lemon oil. Furthermore, key engine components, including the piston head, cylinder head and valves, were coated with a stabilised zirconium catalyst. Experimental evaluation showed that the biofuel-powered engine, equipped with catalysts on these components, exhibited reduced emissions of carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO_x) and particulate matter compared to a conventional engine running on standard fuel. In [6], gaseous fuels such as hydrogen, methane and natural gas were mixed with liquid fuel in a 1:1 ratio for testing purposes, using a platinum-aluminium catalyst in the combustion chamber. The results indicated that the catalytic system effectively reduced NO_x emissions. The addition of hydrogen to the fuel mixture led to increased cylinder pressure, higher NO_x and HC emissions, and reduced smoke, whilst the addition of methane and natural gas contributed to a reduction in NO_x. Furthermore, additional catalytic treatment further reduced smoke levels when using these alternative fuels. In compression ignition (CI) engines, selective catalytic reduction (SCR) systems using urea-based solutions, such as AdBlue [7], are employed to remove NO_x from exhaust gases; however, this approach is associated with high costs and requires frequent refilling. Publication [8] investigated the use of water-in-oil (W/O) emulsions as fuel in compression ignition (CI) engines. The experiments were conducted under controlled operating conditions, at constant engine speed and load, measuring cylinder pressure, heat release rate and exhaust gas composition. The results showed that adding water to the fuel led to a reduction in nitrogen oxide (NO_x) emissions of up to 19.6% and a reduction in exhaust smoke of up to 66.3%. The observed effects are attributed to the phenomenon of micro-explosions of water droplets during combustion, which improves fuel atomisation, enhances air-fuel mixing and lowers peak flame temperatures, thereby reducing NO_x formation and particulate matter generation. According to the authors, this is due to the fact that water lowers the combustion temperature by absorbing heat during evaporation and through micro-explosions caused by the rapid evaporation of water droplets, which simultaneously reduces NOx and smoke emissions. It is also possible to

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produce emulsion fuel using non-biodegradable plastic shopping bags (PGB) [8]. Experiments confirmed that a water-oil emulsion produced from PGB reduces emissions of nitrogen oxides and smoke. The best exergetic efficiency was achieved with an emulsion containing 10% diesel fuel. The study described in [9] analysed the exergetic efficiency of a ZS engine fuelled by biofuel produced from cottonseed oil enriched with titanium oxide and silver nanoparticles. The results suggest that fuels with added nanoparticles exhibit reduced exergy dissipation. It should be emphasised that the addition of nanoparticles entails significant material costs. In [10], cerium oxide was used as an additive to diesel fuel. Experiments showed that the use of this catalyst reduced soot and hydrocarbon emissions by 30% at partial engine load, whilst at full load nitrogen oxide emissions fell by approximately 5%. No significant differences in fuel consumption were observed at medium and maximum loads. Article [11] analysed the effect of alcohol additives (methanol, ethanol, n-butanol and their blends) to diesel fuel on the combustion process. The use of such additives resulted in a reduction in the auto-ignition delay and an improvement in combustion efficiency compared to pure diesel fuel. The best results were obtained for a mixture containing 80% diesel fuel, 10% methanol and 10% n-butanol. In turn, studies [12,13] described the use of a catalyst in injection nozzles in engines with direct mechanical fuel injection. The installation of a platinum catalytic reactor on the inactive part of the injector needle contributed to a reduction in harmful emissions. Article [14] presented a method for the partial dehydrogenation of diesel fuel to produce high-quality hydrogen that could be used in vehicles. The study utilised a platinum catalyst supported on a zinc-aluminium substrate. According to the results of studies [15,16], platinum supported on a zinc-aluminium substrate proved to be an effective catalyst for the dehydrogenation of hydrocarbons. Current trends in the development of internal combustion engines focus on minimising emissions of toxic exhaust components. Studies [17–19] have shown that adding ethanol to fuel contributes to a reduction in NOx emissions. In the studies described in publication [20], the use of powdered biofuel as an additive to the air in the intake system was proposed. Analysis showed that it is possible to use this technology in internal combustion engines without compromising their durability. A solution aimed at improving the chemical properties of the fuel is the use of hydrogen peroxide as an additive. There are many methods for introducing hydrogen into the engine combustion chamber. The most common technique is to install an additional system with a hydrogen cylinder, storing hydrogen in gaseous or liquid form. In this case, hydrogen enters the combustion chamber together with the air. However, the disadvantages of this method are high costs and the need to modify the engine design. An alternative solution is to use a chemical compound that releases hydrogen during combustion – such a compound is hydrogen peroxide. In the presented study, the authors proposed the use of hydrogen peroxide at a concentration of 30%. This additive was used in a quantity of 10% in the fuel mixture. Higher doses may adversely affect the operating parameters of the powertrain and contribute to faster wear of its components. The aim of the additive proposed by the authors is to reduce the amount of toxic substances in the exhaust gases and fuel consumption. Due to its chemical properties, hydrogen peroxide can alter the combustion process of the fuels under investigation and reduce the emission of toxins into the atmosphere via exhaust gases. A review of the literature shows that a great deal of research is being conducted on the modernisation and use of new fuels. In article [21], the authors proposed the use of microemulsification in fuels based on diesel, vegetable oil and alcohol. Research showed that, thanks to the water content, the calorific value of all fuels improved whilst simultaneously reducing emissions of nitrogen oxides and soot. This aims to reduce emissions of carbon dioxide and nitrous oxide, gases responsible for the greenhouse effect. An analysis of the research results presented by the authors [22,23] showed that it is possible to produce oil from non-biodegradable plastic bags (PGB). The authors then proposed preparing a water-oil mixture with the addition of 10% diesel fuel derived from the produced oil. Tests showed that this type of fuel reduced soot and nitrogen oxide emissions in the exhaust. However, fuel consumption increased. Furthermore, the authors did not investigate how the proposed mixture affects the operation of engine components. Article [24] published the results of research on the effect of adding t-butyl peroxide to diesel fuel and biofuel derived from mahua oil and palm oil waste. The experiment

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showed that an engine operating at 100% load exhibited approximately 4% lower emissions of carbon monoxide, unburned hydrocarbons and soot when using diesel with the additive, but approximately 1% higher emissions of nitrogen oxides compared to the biofuel with the additive. The results of an experiment conducted on a single-cylinder, four-stroke ZS engine fuelled with diesel and hydrogen (as the base fuel) and diesel and hydrogen with the addition of di-tert-butyl peroxide (DTBP) are presented in [25]. The 3.50 kW engine operated at a constant speed of 1500 rpm. The article compared the auto-ignition delay period for the given mixtures. The studies showed that the ignition delay decreases with increasing hydrogen and DTBP content in the diesel fuel. Research is being conducted on the use of ethanol as a fuel additive. The results of the experiments are presented in [26,27]. Ethanol lowers the temperature in the combustion chamber, which reduces nitrogen oxide emissions. In [28], the authors described how the addition of hydrogen to diesel fuel and biofuel affects the combustion process in a diesel engine. The analysis showed that hydrogen as an additive not only lowers the temperature in the engine's combustion chamber but also alters the physical and chemical parameters of fuels, particularly those of plant origin. The authors [29] described the effect of 10% hydrogen peroxide as an additive in concentrations of 5%, 10% and 15% to diesel fuel and Calophyllum inophyllum methyl ester. The studies showed that an engine fuelled by biodiesel with the additive generated lower emissions of carbon monoxide and nitrogen oxides. The studies presented in article [30] concern the use of 30% hydrogen peroxide in biofuel made from Jatropha oil. The additive content in the emulsion was 5%, 10% and 15%. The authors analysed engine parameters such as cylinder pressure, ignition delay, ignition duration, heat release and environmental parameters. The analysis showed that the engine achieved the best results at a hydrogen peroxide to fuel mixture ratio of 15%.

The aim of this article is to investigate whether it is possible to reduce exhaust emissions from modern diesel engines by adding hydrogen peroxide to the fuel. A review of the literature has shown that research related to the subject of this article is being conducted in many areas. However, there are few studies concerning the use of hydrogen peroxide in fuels. Research into fuel modification should also be considered in terms of the operation of engine components [31,32]. According to the literature [33], most of the proposed fuel additives do not affect the operation of the fuel supply system nor do they accelerate wear in diesel engines.

2. Materials and Methods

The test fuel was prepared according to the following procedure. Diesel fuel was mixed with 12% hydrogen peroxide in a 10% ratio, using 5% polysaccharide emulsifier in the form of sodium alginate [34]. The role of the emulsifier is to permanently combine two liquids that do not mix. Diesel fuel is non-polar, whereas hydrogen peroxide is polar. These liquids form two separate layers. The emulsifier reduces surface tension, allowing droplets of one phase to disperse within the other. The first stage of the research involved analysing the cetane number of the prepared fuel and the standard diesel fuel from which the mixture was prepared. These tests were carried out on a test bench designed to measure the cetane number in fuel. The fuel under test is compared with a reference fuel using a special single-cylinder ‘ ’ reference engine, in which the compression ratio varies during operation until a specific tendency towards self-ignition, expressed as ignition delay, is reached.

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Figure 1. Test rig for measuring the cetane number of diesel fuel

Engine tests were carried out on a dynamometer using a 4CTI90 – 1BE6 engine with a mechanical fuel supply system. The test rig is equipped with an AVL electric brake, an AVL mass fuel flow meter, a Capelec exhaust gas analyser and a MAHA smoke meter (Figure 2). The measurement error of the test bench is 2%. Exhaust emission tests were carried out in accordance with the Polish standard PN – EN ISO 8178 – 1: 2020 [34].

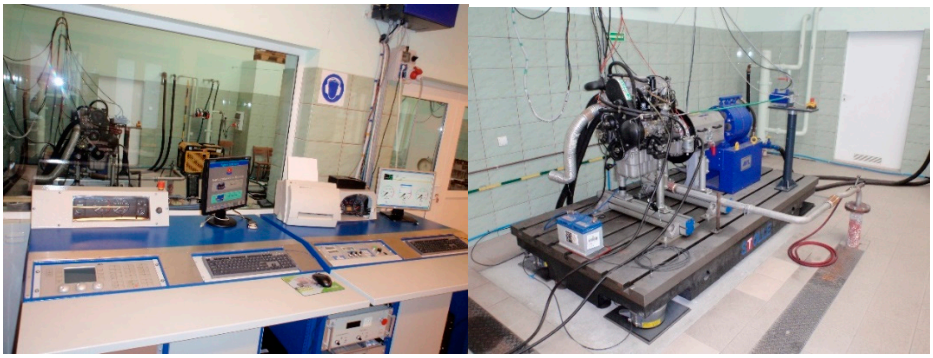

Figure 2. Engine dynamometer with a 4CTI90 – 1BE6 engine and an AVL brake.

Fuel consumption was calculated based on the engine's external characteristics using the following equation:

$$g_e = \frac{3600 \cdot G_e}{N} \quad (1)$$

The following fuels were used in the tests: standard diesel fuel with 12% hydrogen peroxide added in a 10% proportion. The cetane number of the tested fuels was measured on the IDT-69 engine test bench in accordance with the PN-EN ISO 5165 2021- 02 standard. The activation energy of the fuels and the auto-ignition delay time were calculated based on the cetane number. Equation (2) presents the relationship used to calculate the activation energy:

$$E_a = \frac{618.840}{LC + 25} \quad (2)$$

LC – cetane number of the fuel

The auto-ignition delay time of the tested fuels was calculated using equation (3):

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$$\tau_s = (0.36 + 0.22 \cdot c_m) \cdot exp[\, E_a(\frac{1}{RT} - \frac{1}{17.19}) \cdot (\frac{21.2}{P-12.4})^{0.63}] \quad (3)$$

c_m – piston speed,
E_a – activation energy,
R – individual gas constant of the combustible mixture,
T – temperature in the combustion chamber,
P – pressure in the combustion chamber.

During engine testing, the following engine parameters were measured: power, torque, fuel consumption, and emissions of nitrogen oxides, hydrocarbons, particulate matter and carbon dioxide in the exhaust.

The aim of adding hydrogen to the fuel is to reduce the amount of toxic substances in the exhaust gases, such as nitrogen oxides, hydrocarbons and soot. Simplified equations (4–7) illustrate the mechanism of reduction of the above toxic substances.

Equation (4) shows the mechanism for the reduction of nitrogen oxides:

$$2NO + 3H_2O_2 \rightarrow 2N_2 + 3H_2O + O_2 \quad (4)$$

Equation (5) illustrates the mechanism of nitrogen dioxide reduction:

$$2NO_2 + 2H_2O_2 \rightarrow N_2 + 2H_2O + 2O_2 \quad (5)$$

Equation (6) illustrates the general mechanism of hydrocarbon oxidation:

$$C_nH_m + H_2O_2 \rightarrow C_nH_mOH + H_2O \quad (6)$$

Equation (7) shows the general mechanism of particulate matter oxidation:

$$C + H_2O_2 \rightarrow CO_2 + H_2O \quad (7)$$

3. Results

The results of laboratory tests and calculations are presented in Figures 3–11.

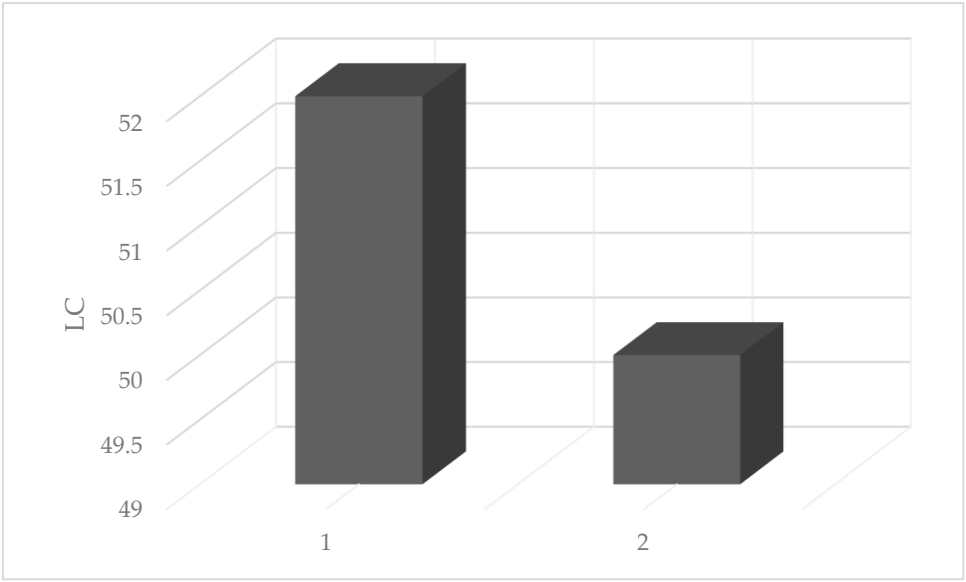

Figure 3. Cetan number of fuels: 1. modified fuel, 2. standard fuel.

The cetane number determines a fuel's tendency to self-ignite. It expresses the percentage content of cetane $C_{16}H_{34}$ in a mixture with α-methylnaphthalene $C_{11}H_{10}$ in the reference fuel, which is equivalent to the fuel under assessment.

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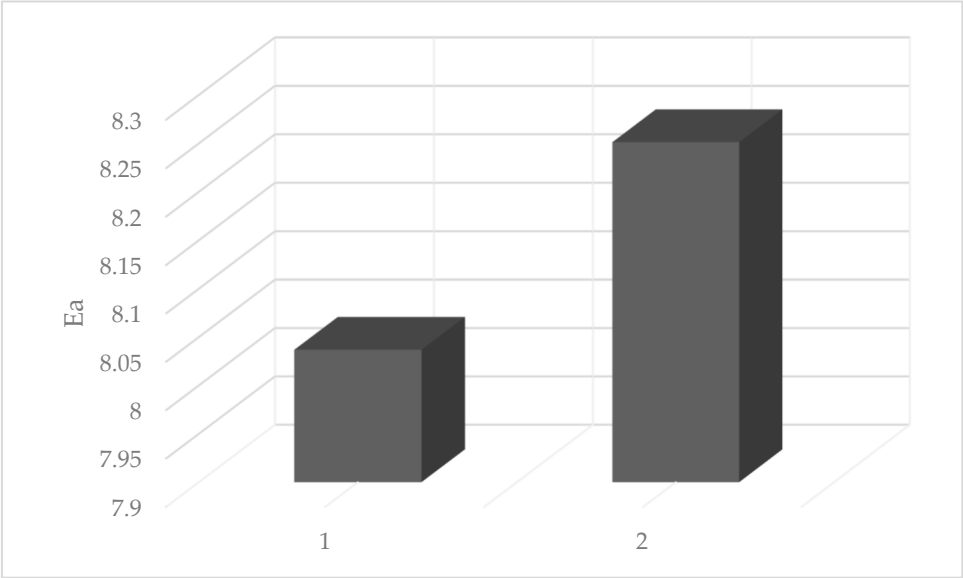

Figure 4. Calculated activation energy: 1. modified fuel, 2. standard fuel.

The factor initiating a chemical reaction is the activation energy (E_a). By definition, this is the energy barrier that the reacting molecules must overcome in order for the substrates to be converted into products. The activation energy value determines the rate of the chemical reaction. The higher the activation energy, the slower the reactions proceed due to the high energy barrier required to carry out the reaction. Factors accelerating chemical reactions are temperature and a catalyst. The activation energy value was calculated using equation (2).

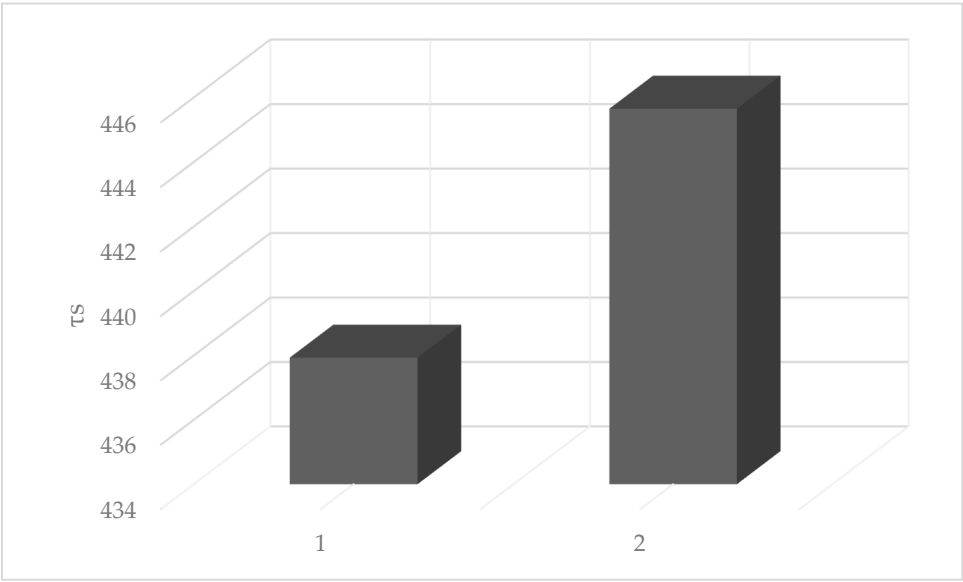

Figure 5. Calculated ignition delays for the fuels tested: 1. modified fuel, 2. standard fuel.

The auto-ignition delay is the time from the injection of fuel into the combustion chamber until the first auto-ignition points of the mixture appear. During this phase, the fuel evaporates and mixes with the air. The shorter this time, the faster and more efficient the combustion process, and the lower the emissions. The auto-ignition delay is calculated using equation (3) [1].

Specific fuel consumption was calculated using equation (1). To determine this value, engine power and instantaneous fuel consumption are required.

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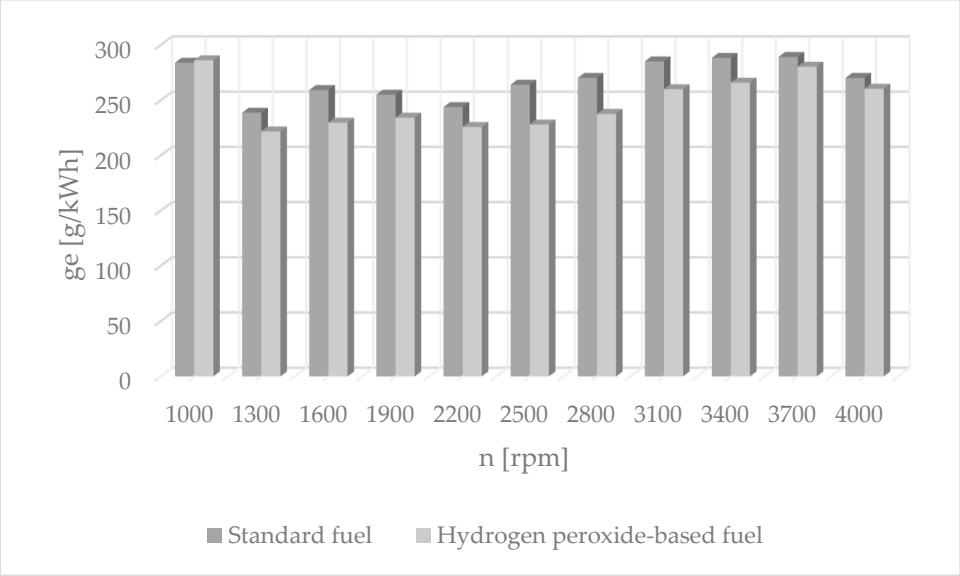

Figure 6. Specific fuel consumption of the engine.

Nitrogen oxides (NOx) are inorganic chemical compounds consisting of nitrogen and oxygen atoms. They are formed during combustion at high temperatures and in the presence of excess air. These compounds are harmful to health – they are toxic and weaken the immune system in the lungs, which increases susceptibility to respiratory tract infections. Long-term exposure to NOx is associated with an increased risk of respiratory diseases. Nitrogen oxide emissions can be reduced by reducing excess air, limiting the amount of heat released, lowering the temperature in the combustion chamber, and using appropriate fuel additives . Furthermore, catalytic converters are often used in exhaust systems, which effectively reduce the NOx content in exhaust gases.

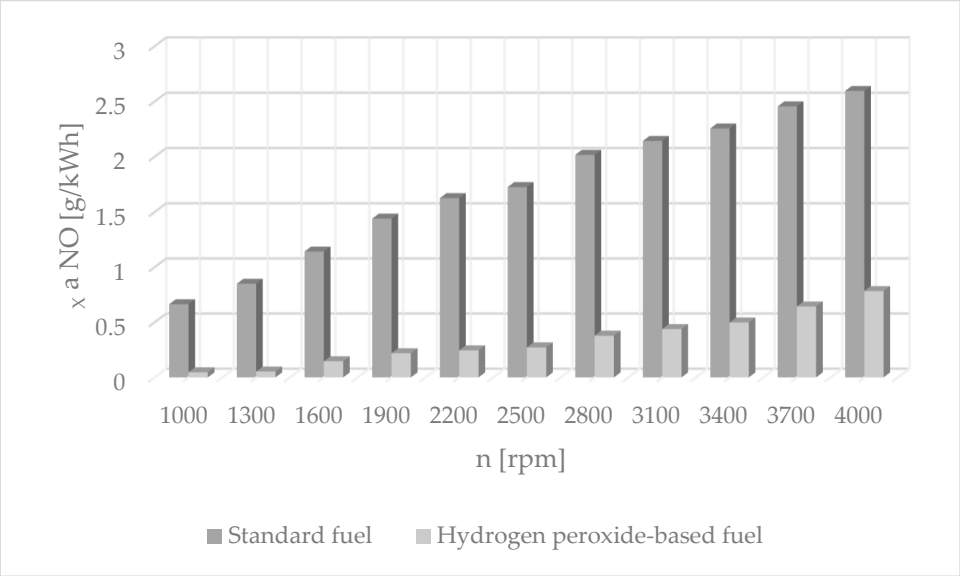

Figure 7. Nitrogen oxide emissions in exhaust gases.

Hydrocarbons (HC) are chemical compounds consisting of carbon and hydrogen atoms. They are produced mainly as a result of incomplete or partial fuel combustion, as well as through the breakdown of hydrocarbon compounds in chain reactions occurring during the combustion of fuel fractions. Their emissions occur particularly near the walls of the combustion chamber, where the temperature is too low to allow soot to form. Long-term exposure to hydrocarbons can lead to serious

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health problems, such as cancer, a weakened immune system, kidney and liver damage, and the development of cataracts.

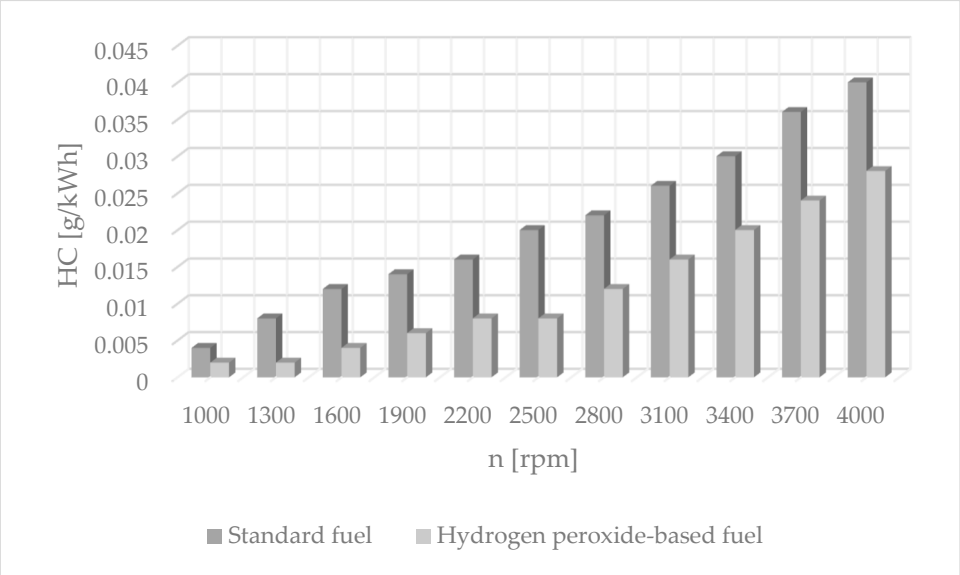

Figure 8. Concentration of hydrocarbon emissions in flue gas.

Carbon dioxide is a gas that is not toxic to living organisms. However, excessive concentrations in the atmosphere cause thermal radiation to be trapped, contributing to the greenhouse effect. For this reason, it is important to take measures to reduce emissions of this carbon compound into the environment.

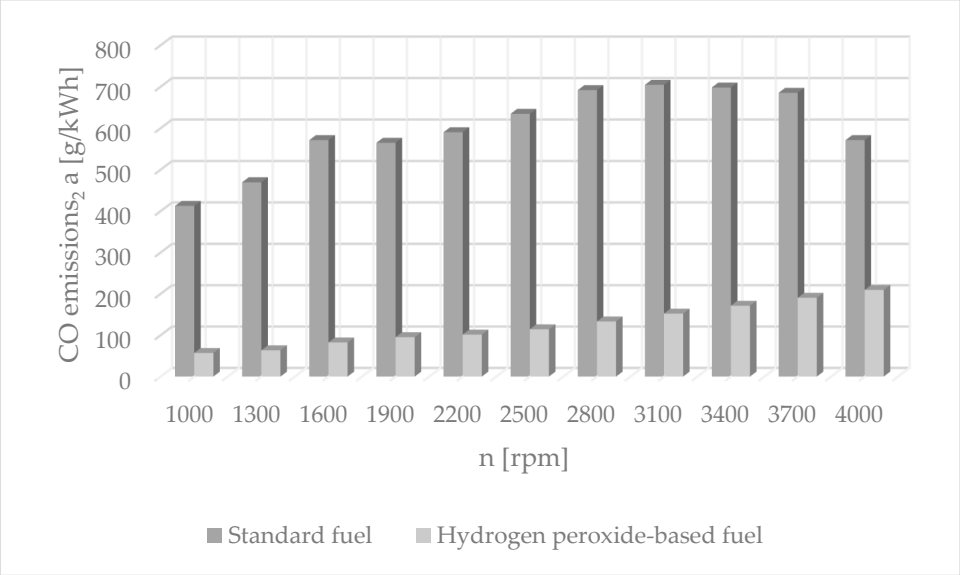

Figure 9. Carbon dioxide emissions in exhaust gases.

Soot, or particulate matter (PM), consists of harmful particles suspended in the air, formed as a result of incomplete fuel combustion. The level of exhaust smoke is most commonly assessed in compression ignition (CI) engines. The main cause of particulate matter emissions is improper fuel atomisation, which negatively affects its evaporation. Soot forms mainly in areas of the combustion chamber where oxygen access is limited. Soot particles can enter the alveoli and subsequently the

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bloodstream, causing respiratory and cardiovascular diseases. Furthermore, soot contains aromatic hydrocarbons, which increase the risk of cancer.

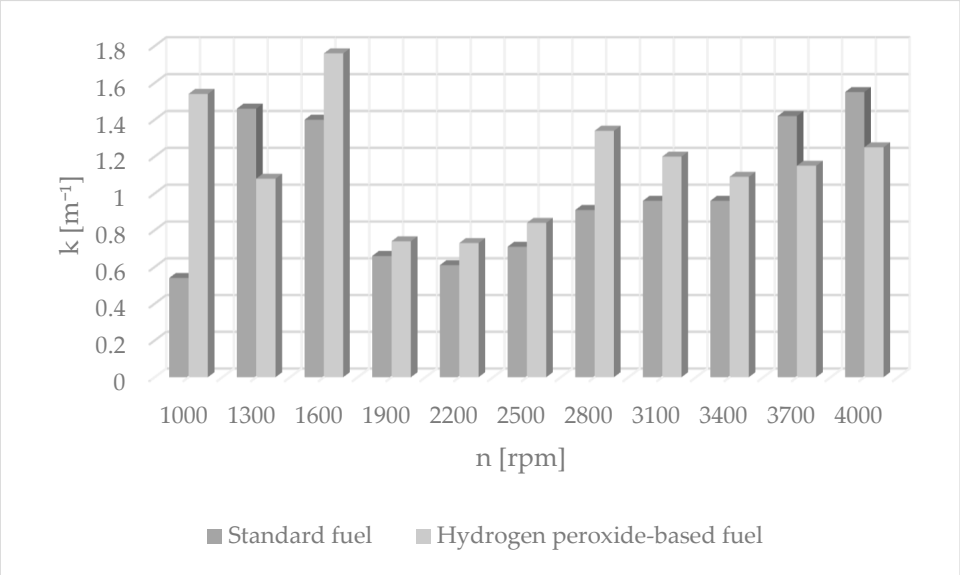

Figure 10. Concentration of particulate matter in exhaust gases.

An important parameter for analysing the processes occurring in the cylinder is the heat of combustion (Figure 11). This parameter determines how fuel additives or the chemical properties of the fuel affect the pressure and temperature in the combustion chamber.

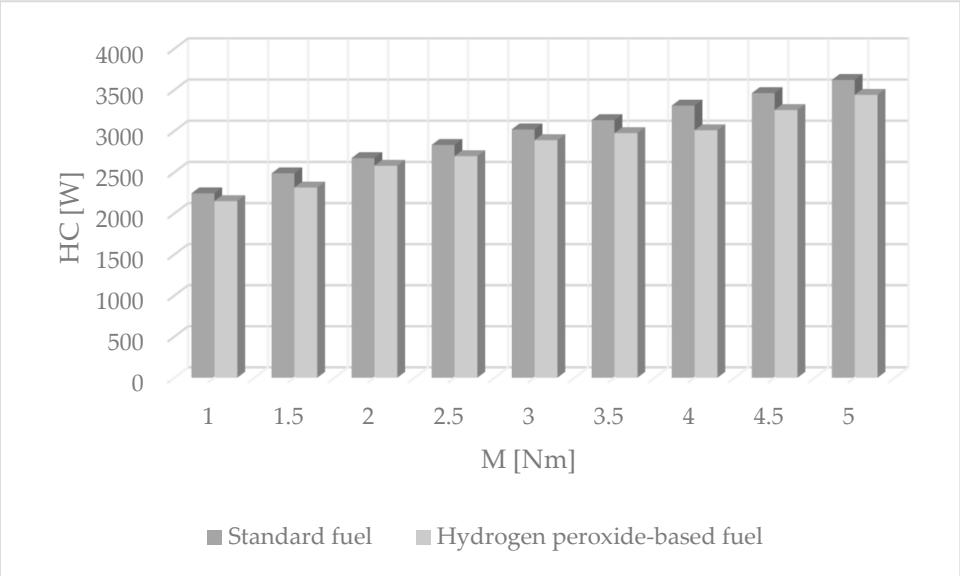

Figure 11. Heat release characteristics as a function of torque.

Modelling of the combustion process of diesel fuel and a mixture of diesel fuel with hydrogen peroxide was carried out in the Matlab environment. The simulation results are shown in Figures 12 and 13.

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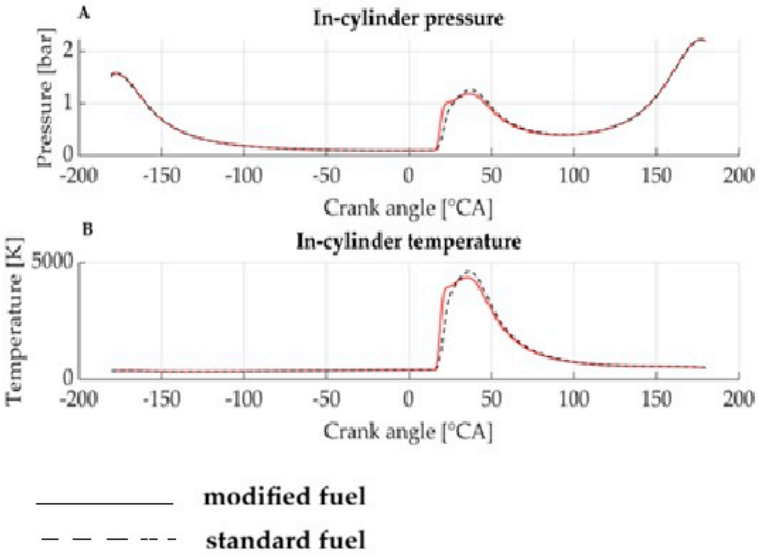

Figure 12. A) Modelled global pressure in the cylinder, B) Modelled global temperature in the cylinder.

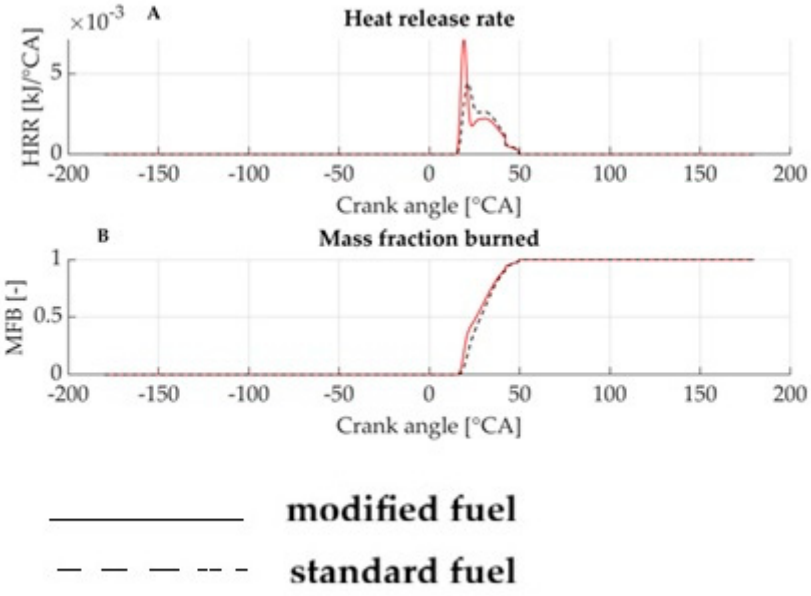

Figure 13. A) Modelled global heat release rate, B) Modelled global mass fraction of burnt fuel.

4. Discussion

The aim of this study was to investigate how a fuel additive in the form of 12% hydrogen peroxide, added in a proportion of 10%, affects the environmental parameters of a modern diesel engine. The course and characteristics of the combustion process in a diesel engine are described in detail in [1].

For the theoretical analysis of the combustion process in this article, a single-zone, zero-dimensional thermodynamic model of a diesel engine was used to analyse the combustion of two fuels: conventional diesel fuel and diesel fuel with a 10% addition of a 12% hydrogen peroxide solution. The model accounts for the effect of additional oxygen introduced via the decomposition of (H_2O), utilising the three-stage Wiebe function and a modified Arrhenius correlation for auto-ignition

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delay [36,37]. The ignition delay was calculated based on the Arrhenius equation extended by the oxygen availability factor OA. This factor determines the extent to which oxygen limits the rate of the chemical reaction (8):

$$\tau_{\mathrm{ID}} = A_s \exp\left(\frac{E_a}{RT_{\mathrm{ref}}}\right)\left(\frac{p_{\mathrm{ref}}}{p_0}\right)^{-n_p} OA^{-k_{OA}} \tag{8}$$

where:
A_s– constant,
E_a– activation energy,
$T_{\mathrm{ref}}, p_{\mathrm{ref}}$– kinetic values at TDC,
n_p– pressure exponent,
k_{OA}– additional oxygen influence exponent,
OA– oxygen availability index.

The oxygen availability (OA) index was introduced to quantitatively determine the relative availability of the oxidiser in the combustion chamber in relation to the stoichiometric oxygen requirement resulting from the fuel dose. This parameter describes the extent to which the fuel-air mixture is oxygen-lean or oxygen-rich, and allows for the influence of oxygen additives such as hydrogen peroxide (H_2O_2) (9)

$$OA = \frac{m_{O_2,\mathrm{powietrze}} + m_{O_2,H_2O_2}}{m_{O_2,\mathrm{stoich}}} \tag{9}$$

where:

- $m_{O_2,\mathrm{powietrze}}$– the mass of oxygen contained in the intake air (a mass fraction of 21% oxygen is usually assumed),
- m_{O_2,H_2O_2}– additional mass of oxygen released as a result of the exothermic decomposition of hydrogen peroxide according to the reaction

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \tag{10}$$

- $m_{O_2,\mathrm{stoich}}$ – the theoretical (stoichiometric) amount of oxygen required for the complete combustion of the mass of injected fuel with a known stoichiometric AFR_{st} .

Values of the '$OA > 1$ ' index indicate increased oxygen availability relative to stoichiometric conditions, which promotes a reduction in ignition delay, more intense premixed combustion and a faster progression of the high heat release phase. Conversely, values of '$OA < 1$ ' indicate an oxygen deficiency, which promotes a longer ignition delay, a weaker premix phase, a prolonged diffusion combustion phase, and increased soot emissions.

The use of the OA index allows the influence of hydrogen peroxide to be taken into account both through increased oxygen availability and through the thermal effect resulting from its exothermic decomposition. This parameter is particularly useful in simplified zero-dimensional models, where it allows the changes in mixture reactivity following the introduction of oxygen additives to be modelled without the need for complex kinetic models.

Combustion in the model was modelled using the sum of three Wiebe functions, describing respectively:

- the premixed burn phase,
- the mixing-controlled phase (mixing-controlled / diffusion burn),
- the late burn phase.
- Each of the three stages is described by a classical Wiebe function.

The total mass fraction burned (MFB) is expressed as the weighted sum of the three Wiebe functions: (11):

$$MFB(\theta) = E_1 M_1(\theta) + E_2 M_2(\theta) + E_3 M_3(\theta) \tag{11}$$

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where E_1 , E_2 , E_3 denote the energy contributions corresponding to the premix phase, the mixing-controlled phase and the late burn phase, respectively.

The Wiebe function for the stage i takes the form (12):

$$M_i(\theta) = 1 - \exp\left[-\left(\frac{\theta - SOC_i}{\Delta\theta_i}\right)^{m_i+1}\right] \quad (12)$$

where:

a_i – shape factor,

m_i – the Wiebe exponent,

$\Delta\theta_i$ – duration of the combustion stage,

SOC_i – start of the combustion stage.

The derivative of the Wiebe function describes the combustion rate, and when multiplied by the total reaction energy, it determines the heat release rate (HRR) (13), (14):

$$\frac{dM_i}{d\theta} = \frac{a_i(m_i+1)}{\Delta\theta_i}\left(\frac{\theta - SOC_i}{\Delta\theta_i}\right)^{m_i} \exp\left[-a_i\left(\frac{\theta - SOC_i}{\Delta\theta_i}\right)^{m_i+1}\right] \quad (13)$$

$$HRR(\theta) = Q_{\text{total}}\left(E_1\frac{dM_1}{d\theta} + E_2\frac{dM_2}{d\theta} + E_3\frac{dM_3}{d\theta}\right) \quad (14)$$

where Q_{total} takes into account the combustion energy of diesel fuel and the energy released during the exothermic decomposition of H_2O_2.

The start of combustion (SOC) was defined as the sum of the start of fuel injection (SOI) and the ignition delay (ID). The characteristic combustion angles were determined in accordance with the standard MFB definition:

MFB(CA10) = 0.1,

MFB(CA50) = 0.5,

MFB(CA90) = 0.9.

The CA50 parameter serves as the main measure of combustion phasing, whilst CA10 and CA90 indicate the start and end of the main combustion phase, respectively.

The decomposition of H_2O_2 generates additional heat of approximately 95–100 kJ/mol, which increases the reaction rate in the initial combustion phase and enhances the Wiebe derivative ($\frac{dM}{d\theta}$) in the premixed region.

This has been taken into account in the model by:

- increasing the proportion of energy in the premix phase,
- shortening its duration,
- increasing the shape factor a_1 , which corresponds to a more rapid, intense phase of volumetric combustion.

Wiebe's three-stage model, supported by the OA relationship that modifies the ignition delay, provides a compromise between computational complexity and the accuracy of representing combustion trends in compression-ignition engines. This model captures the key characteristics of the combustion process and enables the analysis of the effect of H_2O_2 addition on combustion dynamics without the need for advanced chemical kinetics.

An analysis of the test results shows that nitrogen oxide emissions were lower for the modified fuel across the entire speed range, whilst the modelled heat release rate was higher. The difference stems from the fact that H_2O_2 increases the amount of water, whilst the simplified model does not account for the increased water content in the engine combustion chamber. During the combustion process, the medium within the engine's working space is not homogeneous. There are areas with higher and lower temperatures. The overall higher HRR does not imply a higher global temperature in the engine chamber; consequently, the NO_x content has decreased, which is typical for fuels mixed with water vapour. At minimum engine loads, the combustion temperature is low. Under such engine operating conditions, unfavourable conditions prevail in the cylinder working space:

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- fuel atomisation is poorer,
- fuel evaporation is slower,
- formation of the combustible mixture is poorer,
- H_2O molecules increase the cooling of the fuel stream,
- fuel-rich zones are formed.

Such an environment promotes the formation of soot during combustion. Therefore, when analysing the characteristics of soot emissions during tests at minimum engine speeds, they are higher for the modified fuel. Only when the engine begins to operate at medium and maximum loads does the soot content decrease compared to standard fuel. This is because:

- the combustion temperature rises,
- mixing is more intense,
- soot oxidation is more effective,
- the decomposition products of hydrogen peroxide oxidise soot more rapidly.

Soot undergoes oxidation at higher temperatures and with a higher oxygen content. At low engine loads, there is a shortage of oxygen and a lower temperature [38].

5. Conclusions

Analysis of the test results shows that the use of hydrogen peroxide as a fuel additive in a diesel engine mainly affects emissions of nitrogen oxides, hydrocarbons and carbon dioxide. When analysing the environmental parameters of engine operation, it can be observed that hydrogen peroxide slightly increases the soot content in the exhaust gases. Soot is crystallised carbon that forms at low temperatures.

Laboratory tests have shown that the use of a 10% additive of a 12% hydrogen peroxide solution increased the fuel's cetane number from approximately 50.0 to 52.0. The increase in the cetane number reduced the activation energy of the combustion reaction and shortened the auto-ignition delay time, which contributed to a more stable combustion process in the diesel engine.

Tests carried out on an engine dynamometer demonstrated a significant impact of the hydrogen peroxide additive on the engine's environmental performance. In particular, a reduction in nitrogen oxide (NOx) and unburned hydrocarbon (HC) emissions was observed across a wide range of engine crankshaft speeds. This effect can be explained by the presence of additional oxygen and hydrogen in the fuel, which intensify oxidation reactions and lower local combustion temperatures, thereby promoting NOx reduction.

At the same time, the test results showed a slight increase in particulate matter (soot) emissions, which may be due to changes in the diffusion combustion and afterburning phases, as well as modifications to the fuel atomisation conditions in the combustion chamber. Carbon dioxide emissions did not change significantly, indicating that the addition of hydrogen peroxide does not worsen the CO_2 emissions balance or the engine's energy efficiency.

It should be emphasised that the proposed solution does not require any modification to the engine design or the use of costly external hydrogen supply systems, which is a significant advantage from the point of view of practical application. Further research should focus on long-term engine operation and the effect of the additive on the durability of fuel system components and the combustion chamber.

The next stage of research into the possibility of reducing particulate matter in exhaust gases will involve the use of modified fuel injectors in an engine fuelled with the presented fuel additive.

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