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Ryszard ZADRĄG
Paweł SOCIK
Marcin ZACHAREWICZ
Artur BOGDANOWICZ
Norbert SIGIEL

Combustion Engines
Polish Scientific Society of Combustion Engines

Analysis of biodegradable additives in marine fuels and their effect on toxic exhaust emissions

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This study investigates the influence of biodegradable additives, specifically butyl alcohol, ethyl alcohol, and demineralized water, on the emission of toxic compounds from marine diesel engines. Experiments were conducted using a Sulzer 6AL20/24 engine fueled with conventional diesel and two fuel blends containing alcohols and water. Emissions of NO_x, CO, CO_2, and O_2 were measured and analyzed via statistical modeling. Results indicate that component fuels can reduce NO_x emissions by up to 7.5%, mainly due to the cooling effect of water in the fuel mixture. However, effects on CO emissions were less consistent, varying with engine load and fuel composition. CO_2 emissions remained similar across fuels, while the presence of oxygenated compounds influenced oxygen levels. The findings support the potential of biodegradable fuel additives in reducing marine engine emissions. However, further studies are necessary to optimize combustion and meet environmental regulations.

Key words: *marine diesel combustion engine, biodegradable fuels, butanol, exhaust emissions, emission modelling*

1. Introduction

Maritime transportation is a major pillar of the global economy, accounting for about 80% of global trade by volume [26, 32]. The operation of internal combustion engines on vessels involves significant emissions of pollutants, including nitrogen oxides (NO_x), sulfur oxides (SO_x), particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs) and other toxic compounds [21, 22]. These compounds have negative effects on both human health and the environment, contributing to climate change, acidification of ecosystems and degradation of air quality in coastal areas [31].

The International Maritime Organization (IMO) is introducing increasingly stringent standards for the emissions of harmful compounds from reciprocating internal combustion engines, including restrictions on NO_x (Fig. 1) and SO_x emissions (MARPOL Annex VI agreement, including Tier I, II and III standards) [16, 32, 33]. The IMO is not the only organization placing restrictions on toxic emissions. The EPA (U.S. Environmental Protection Agency) is introducing stricter standards for particulate matter (PM), nitrogen oxides and carbon dioxide (Tier IV) emissions – a 60% reduction from the previous standard [34]. The European Union is not lagging behind EPA regulations. The EU is introducing further restrictions on carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO_x) and particulate matter emissions – the Stage 5 document [3, 16]. The document talks about a 72% reduction in nitrogen oxides and hydrocarbon emissions compared to Stage IIIa, and a 93% reduction in PM. One should not forget the global player, the People's Republic of China. China currently has Stage 2 regulations, which are very similar to EPA Tier 3 [3].

With standards being introduced, there is growing interest in alternative fuels and additives that can reduce exhaust gas toxicity [35]. One area of intense research is biodegradable fuel additives, including fatty acid methyl esters (FAMEs), higher alcohols (e.g., butanol), ethers or biopolymers [1, 29].

Studies have shown that the use of biodegradable fuel additives can lead to reductions in emissions of particulate matter, hydrocarbons and PAHs, mainly through improved combustion and higher oxygen content in the fuel mixture [13, 15, 20]. The effect of such additives on the emission of NO_x and other toxic components of exhaust gases under the operating conditions of marine engines is still not clearly defined, especially considering the specificity of loads and the variety of engine types used in shipping [8, 29].

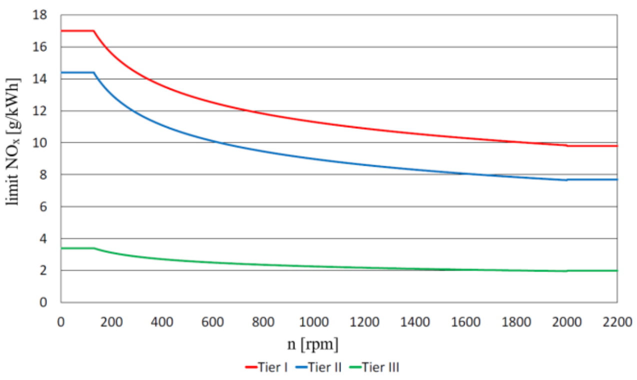

Fig. 1. Maximum allowable NO_x emissions according to MARPOL regulations with a breakdown into Tier I, II and III standards depending on nominal engine speed [32, 35]

The purpose of this study is to analyze the possibility of using biodegradable additives (butyl alcohol, methyl alcohol, demineralized water) in marine fuels and to evaluate their impact on the emission of toxic compounds in the exhaust gas of marine internal combustion engines. Particular emphasis was placed on the compounds of greatest environmental and health importance, such as NO_x and CO.

The results of the study can make an important contribution to the process of adapting shipping to increasingly stringent emission standards, and are a continuation of the authors' previous work [6, 7, 30].

2. Characteristic of harmful compounds emitted by engines

Exhaust gas is formed by the oxidation of hydrocarbons contained in the fuel with oxygen from the air. Under actual conditions, the combustion process is partial and incomplete, leading to the emission of products (Fig. 2) such as nitrogen oxides (NO_x), carbon oxides (CO_x), unburned hydrocarbons (HC), particulate matter (PM) and sulfur oxides (SO_x) [13]. The proportion of toxic components is 0.2–0.26% of the exhaust mass, with total specific emissions reaching 16–22 g/kWh [23, 25]. When operating a marine engine at a nominal power of 50,000 kW, the mass of toxic substances emitted will be 20–25 tons per day.

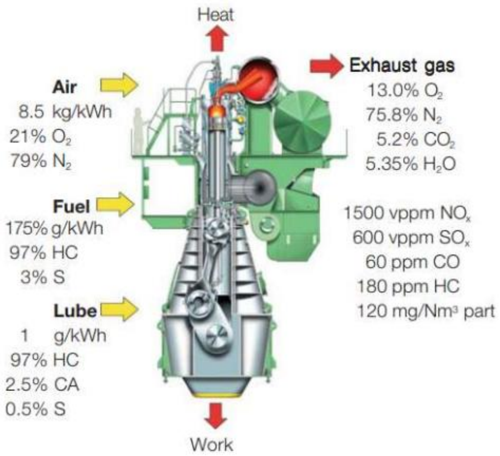

Fig. 2. Flow process and typical exhaust gas composition from marine engines [11]

Nitrogen oxides are formed by the reaction of nitrogen with oxygen at high temperatures. The concentration of nitrogen oxides increases exponentially relative to the maximum combustion temperature [23]. Mechanisms of NO_x formation include the Zeldovich model (thermal), the Fenimore mechanism (so-called fast NO) and the process of NO_x formation from nitrogen contained in the fuel [23]. NO_x emissions in medium-speed engines are about 13.8 g/kWh (59 kg/ton), and in slow-speed engines they reach 18.7 g/kWh (84 kg/ton) [16, 17, 23, 25, 27] NO_x compounds have high toxicity – nitric oxide (NO) has an affinity for hemoglobin 1.500 times greater than oxygen, which limits the blood's ability to carry oxygen [23]. NO_2 concentrations above 0.12 mg/dm³ cause irritation of mucous membranes, and at 0.38–1.33 mg/dm³ can lead to death [19, 23].

Carbon monoxide is formed under conditions of local oxygen deficiency ($\lambda < 1$), low load and underheating of the engine, and as a result of late injection or improper fuel atomization [23]. For marine reciprocating engines, CO emissions average 1.8–2.1 g/kWh [14]. CO binds to hemoglobin about 210–300 times more strongly than oxygen, causing hypoxia [12, 14, 17, 18, 21, 23].

Unburned hydrocarbons in the flue gas are formed as a result of incomplete combustion, as well as wall and gap effects. The crevice effect is related to the extinguishing of the flame in the narrow spaces between combustion chamber components [27]. HC emissions are about 0.5–0.6 g/kWh [23, 27] and increase in proportion to lubricating oil consumption – a doubling of consumption results in a 6–18% increase in HC emissions [23]. Unburned hydrocarbons have irritant and toxic effects, leading to, among other things, damage to the bone marrow and circulatory system [12, 23].

Particulate matter (PM) consists of both soluble fractions (SOF), containing heavy aromatic and aliphatic hydrocarbons, and insoluble fractions, which are dominated by soot, sulfates and metals from fuel and wear products of engine components [13]. Soot forms under conditions of local oxygen deficiency at temperatures of 1900–2300 K, reaching a diameter of 0.1–0.5 μm as early as about 1 ms after the onset of combustion [23]. The proportion of oil-based particles in the total PM mass varies from 2% to as much as 40%, depending on the source [23, 27]. Although soot itself is not highly toxic, its porous structure makes it adsorb other toxic compounds, making it particularly dangerous to the respiratory system [19, 23].

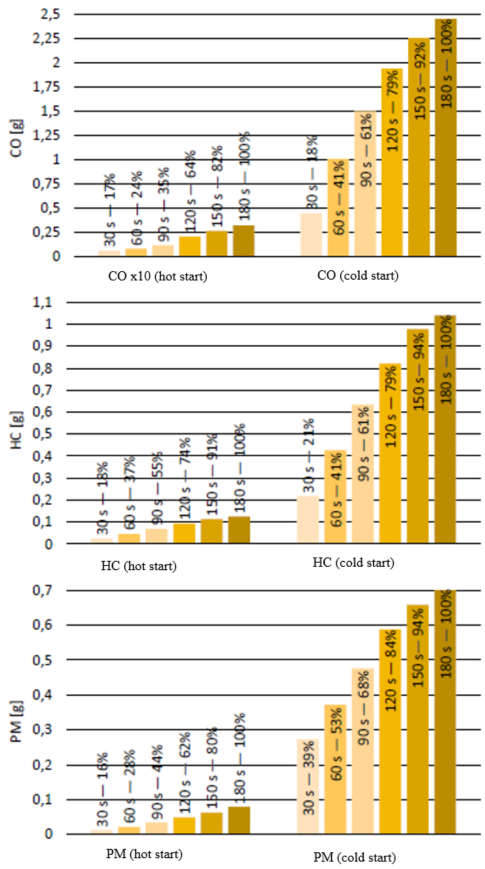

Fig. 3. Comparison of the contribution of individual operating periods to the total emissions during idle running (cold start) [4]

Sulfur oxides (SO_x) are formed by the oxidation of sulfur contained in fuel. The predominant product is SO_2, of which 2–4% is oxidized to SO_3, forming sulfuric acid in the atmosphere and contributing to acid precipitation [19, 23]. SO_2 emissions are calculated according to the relationship: eSO_2 = 20%S [kg/ton of fuel] or eSO_2 = 4.2%S [g/kWh], where %S is the mass proportion of sulfur in the fuel [21, 23]. It is interesting to note that increased sulfur content in the fuel may contribute to a decrease in NO_x emissions, since sulfur takes up some of the available oxygen, reducing its contribution to the formation of nitrogen oxides [23, 30].

The thermal condition of the engine has a significant impact on emissions. During a cold start, CO, HC and PM emissions are many times higher than during a hot start. In the first 60 seconds of cold engine operation, up to 53% of the total PM emissions are produced, and about 41% of CO and HC emissions are related to the entire 180-second duty cycle. For a hot start, emissions are stable and much lower (Fig. 3) [2, 23].

3. Alternative fuels used in compression-ignition piston internal combustion engines

In the context of reducing emissions of toxic exhaust components from compression-ignition reciprocating internal combustion engines, alternative fuels, including alcohols as biofuels, are becoming increasingly important. The use of these fuels is driven by the need to meet increasingly stringent emission standards [18, 23].

Alcohol fuels, such as ethanol and butanol, are being researched because of their aerobic properties, which promote improved combustion, reducing hydrocarbon (HC) and carbon monoxide (CO) emissions. Ethanol has a high cetane number and a good ability to mix with diesel fuel. However, its use leads to a lower heating value of the fuel mixture. It requires appropriate modifications in the design of the engine injection system [23, 30]. Butanol, thanks to its higher calorific value and lower hygroscopicity compared to ethanol, is a more favorable component for creating fuel mixtures. In contrast, its share in the mixture can significantly affect the stability of engine operation and combustion parameters [10, 23, 30]. The use of alcohols also requires consideration of their effect on the physicochemical properties of the fuel, such as viscosity, density and flash point, which directly affects the performance of the fuel system and the dynamics of the combustion process [10, 23].

In parallel, work is being carried out on the use of biofuels, particularly higher fatty acid methyl esters (FAME), which are mainly made from vegetable oils such as rapeseed oil. Biofuels of this type have a high oxygen content, which is conducive to reducing CO and HC emissions, as well as lowering exhaust smoke emissions. Nevertheless, an increase in nitrogen oxide (NO_x) emissions is observed under certain engine operating conditions, due to the higher combustion temperature of the fuel-air mixture and the presence of oxygen in the structure of the fuel molecules [11, 17, 23, 28]. Methyl esters exhibit a lower heating value compared to diesel fuel, as well as higher viscosity and density, which affect the characteristics of the fuel injection process and its atomization in the combustion chamber [9, 23]. Also important are the performance characteristics of biofuels, such as susceptibility to oxidation, hygroscopicity and corrosive properties, which may limit their long-term use without requiring changes in the design of fuel supply systems [10, 23].

The results of the study indicate that the use of rapeseed oil methyl esters (REE) and ethyl alcohol (EtOh) in the developed BIOXDIESEL fuel (variants M1 to M4 – shown in Table 1) by Struś [28] leads to a slight reduction in the indexed power and torque of CI engines, which is a consequence of the lower calorific value of these fuels compared to conventional diesel fuel. At the same time, a favorable effect of biofuels on the reduction of exhaust smoke emissions, stability of engine operation and reduction of emissions of particulate matter, carbon monoxide and unburned hydrocarbons is observed, confirming their potential in reducing toxic emissions [5, 11, 18, 28]. However, in the case of biodegradable fuels, it is necessary to take into account the increase in NO_x emissions, which poses a significant challenge in terms of meeting current emission standards [5, 16, 28].

Table 1. Comparison of physicochemical properties of varieties of Bioxdiesel fuel and diesel oil, where M1 70% DF + 30% REE, M2 70% DF + 4% EtOh + 26% REE, M3 70% DF + 6% EtOh + 24% REE, M4 70% DF + 10% EtOh + 20% REE [8]

Property	DF	M1	M2	M3	M4
Density T_0 = 15 °C [kg/dm³]	0.835	0.848	0.845	0.844	0.840
Kinematic viscosity T_0 = 40 °C [mm²/s]	2.66	3.52	2.40	2.40	2.33
Cetane index	52.5	51	50.5	50	49
Flash point [°C]	65	58	32	26	22
Cloud point [°C]	-16	-15	-19	-23	-22
Cold filter plugging point (CFPP) [°C]	-31	-29	-33	-34	-37
Pour point [°C]	-40	-35	-37	-38	-41
Water content in fuel [mg/kg]	44.4	66	92.4	97.1	103

To summarize, the use of alternative fuels, both alcohol and biofuels, is an important research direction for reducing emissions of harmful compounds from marine reciprocating internal combustion engines. Despite some operational and technological limitations, these fuels allow significant reductions in emissions of selected toxic components of exhaust gases, which can be of significant importance in the context of the implementation of environmentally friendly strategies in marine transportation [5, 23, 28].

4. Research plan and research object

4.1. Research plan

The research was carried out according to a simplified experiment plan. The simplified experiment plan contains 9 combinations resulting from 3 input quantities, where each quantity (speed – n, torque – M, fuel mixture – PAL) can take integer values in the range $\langle -1, 1 \rangle$. Based on previously conducted studies [6, 7, 30], the values of the parameters constituting a simplified experimental plan were determined. The assumed values of the input parameters are shown in Table 2, where the name of the fuel that was fed to the engine during the test is denoted by PAL. Three types of fuel were supplied to the engine: diesel fuel and two mixtures containing diesel fuel (DF), butyl alcohol (BOh), ethyl alcohol (EtOh), and water (W). The fuels used in the

test contained the following volume percentages of the individual components:
– DF 100% DF
– M1 60% DF, 35% BOh, 3% EtOh, 2% W
– M2 60% DF, 35% BOh, 1% EtOh, 4% W.

Table 2. The experimental plan

Test	A	B	C	n [rpm]	M [kNm]	PAL
1	0	1	–1	700	4.62	DF
2	1	1	1	750	4.62	M2
3	0	0	0	700	2.96	M1
4	1	0	–1	750	2.96	DF
5	0	–1	1	700	0.98	M2
6	–1	0	1	650	2.96	M2
7	1	–1	0	750	0.98	M1
8	–1	1	0	650	4.62	M1
9	–1	–1	–1	650	0.98	DF

The experimental plan was chosen due to its high cost-effectiveness. It is particularly advantageous when measurements are expensive and must be limited to only those strictly necessary. Using this plan, the researcher was able to conduct as few as nine tests, which nevertheless allowed for a satisfactory analysis of the obtained results. In this plan [7, 30]:
– A represents the crankshaft rotational speed
– B represents the torque
– C represents the fuel mixture.

The coded levels −1, 0, and +1 indicate the lowest, intermediate, and highest values of parameters A, B, and C, respectively [7, 30].

The output values are all recorded for engine and exhaust parameters. For the study, the following output parameters were determined:
– exhaust gas temperature $t_{exh.}$ [°C]
– nitrogen oxides concentration in the exhaust gas NO_x [ppm]
– nitrogen oxide concentration in the exhaust gas NO [ppm]
– nitrogen dioxide concentration in the exhaust gas NO_2 [ppm]
– carbon monoxide concentration in the exhaust gas CO [ppm]
– carbon dioxide concentration in the exhaust gas CO_2 [%].

4.2. Research object and measurement equipment

The tests were conducted on a Sulzer 6AL20/24 compression-ignition engine (Fig. 4), which features an in-line cylinder arrangement and a four-stroke cycle. The engine has four valves per cylinder, direct fuel injection and is turbocharged. The basic specifications of the engine are shown in Table 3. The engine is coupled to a Froudea-type DPY6D hydraulic brake.

The composition of the exhaust gas was recorded using a Testo 350 electrochemical analyzer. The concentration values of a given substance in the exhaust gas were monitored and recorded using the software supplied with the analyzer. The Testo 350 analyzer can measure the following compounds: O_2, CO_2, CO, NO, NO_2, SO_2.

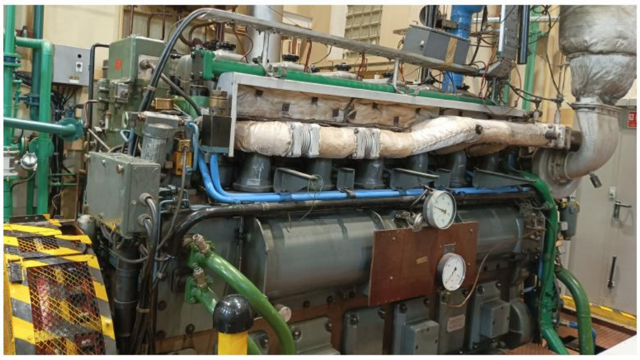

Fig. 4. Laboratory engine stand

The engine's operating parameters were recorded by a set of measuring instruments installed in the intake, exhaust, oil and cooling systems.

Table 3. Technical data of the engine used in the tests

Configuration	6L, 4-S
Rated power	420 kW
Rated speed	750 rpm
Compression ratio	12.7
Mean effective pressure	1.47 MPa
Mean piston speed	6 m/s
Piston stroke	240 mm
Cylinder bore	200 mm
Specific fuel consumption	212 g/kWh

5. Results

5.1. Test results

During the tests conducted, the differences of ambient temperature and pressure values for all measurement points did not exceed 5%. Thus, further calculations were referred to averaged values, i.e. an ambient temperature of 20°C and an ambient pressure of 1013 hPa. The emission values of O_2, CO_2, CO and NO_x compounds were calculated as the arithmetic average of the recorded values at the time of measurement, with the average NO_x being the sum of the average NO and NO_2. The concentration of SO_2 in the flue gas was not determined due to the negligibly small proportion of sulfur in the fuel.

The mass emission of a given substance in the exhaust was calculated using the following formula:

$$E_x = u_x \cdot c_x \cdot \dot{m}_{spal} \tag{1}$$

where: E_x – mass emission rate of substance $[\frac{kg}{s}]$, u_x – conversion factor for substance x [23], c_x – concentration of substance x in the exhaust gases, expressed in [%] for O_2 and CO_2, and in [ppm] for CO and NO_x, $\dot{m}_{spal}$ – exhaust gas mass flow rate $[\frac{kg}{s}]$.

The specific emission of the given substance was calculated according to the following formula:

$$e_x = 3.6 \cdot 10^9 \cdot \frac{E_x}{P_e} \quad (2)$$

where: e_x – specific emission of substance x $[\frac{g}{kWh}]$, P_e – useful power output [W].

The averaged emission values of oxygen, carbon dioxide, carbon monoxide, and nitrogen oxides are presented in Tables 4 and 5.

Table 4. Average emission values at measurement points

Measurement point (n/M/PAL)	c_{NO_x} [ppm]	c_{CO} [ppm]	c_{O_2} [%]	c_{CO_2} [%]
650/2.96/M2	1471	190	11.07	6.94
750/4.62/M2	1409	158	11.30	7.21
700/2.96/M1	1528	137	11.82	6.83
650/4.62/M1	1355	459	10.30	7.65
750/2.96/DF	1448	143	12.02	6.71
750/0.98/M1	1049	175	12.98	5.67
650/4.62/DF	1492	344	10.73	7.67
700/0.98/M2	1110	209	13.08	5.63
650/0.98/DF	1188	241	13.00	6.02

5.2. Emissions model

Based on the collected measurement data, a statistical analysis was performed using the Statistica 8.0 software. The program was supplied with measurement results of harmful exhaust gas emissions, including concentrations of NO_x, CO, O_2, and CO_2, as well as engine operating parameters such as rotational speed, torque, and the type of fuel used. Statistica enabled the development of extrapolation models describing the emission values of the analyzed substances as a function of the input variables.

A linear-quadratic model was applied in the analysis. Compared to other models, the selected model was characterized by high coefficients of determination (R^2) and low mean square errors (MS). The final model equations took the form of a polynomial consisting of seven monomials with the greatest impact on the output value.

The variables included in the models comprised both linear terms (n, M, PAL) and quadratic terms (n^2, M^2, PAL^2), as well as linear-linear interactions ($n \cdot M$, $n \cdot PAL$, $M \cdot PAL$), linear-quadratic interactions (e.g. $n^2 \cdot M$, $M^2 \cdot PAL$), and quadratic-quadratic interactions (e.g. $n^2 \cdot M^2$).

The accuracy of the models was evaluated based on plots comparing the approximated values with the actual measured values; the closer the points were located to the regression line, the better the model fit was considered to be. For a more comprehensive analysis, three-dimensional plots were generated to illustrate the relationship between the emissions of individual compounds and the engine's rotational speed, torque, and the specific fuel type (PAL). Pareto charts were prepared to assess the influence of individual monomials on the emission values.

Rotational speed values were adopted in the range of 650–750 rpm. At the same time, the water content in the fuel was selected from the set {0%, 2%, 4%}, with constant torque values of {0.98, 2.96, 4.62}.

5.3. Analysis of nitrogen oxide concentrations

The conducted analysis of the influence of engine rotational speed, torque, and the type of fuel combusted on nitrogen oxides (NO_x) emissions demonstrated that the torque generated by the engine has the greatest impact on NO_x emissions (Fig. 5). Higher torque leads to an increase in the mean effective pressure and a larger fuel dose, which raises the combustion temperature and promotes higher NO_x emmisions. The notation (Fig. 5) "L" indicates that the coefficient value is assigned to the linear term of the polynomial, "Q" – to the quadratic term, and "by" – in relation to a reference value.

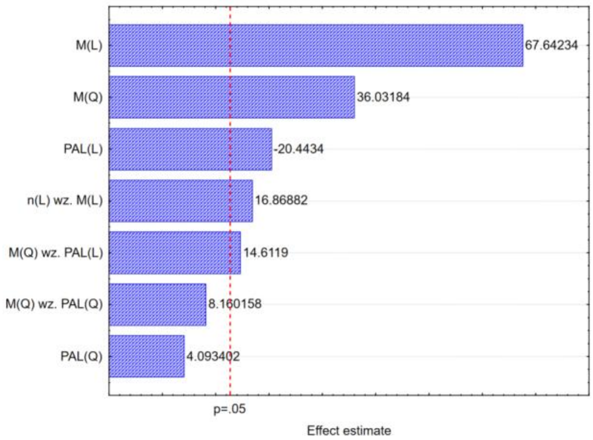

Fig. 5. Pareto charts of effect for NO_x

The type of fuel also has a significant impact on nitrogen oxides (NO_x) emissions, both as an independent variable and through interactions with engine torque. It was shown that a higher water content in the fuel mixture (M2 – 4% water) at lower engine loads (M < 3 kNm) results in a reduction of NO_x emissions by approximately 100 ppm compared to conventional diesel fuel. However, at higher

Table 5. Average values of mass emission intensity and unit emission of compounds: at measurement points

Measurement point (n/M/PAL)	E_{NO_x} [kg/h]	E_{CO} [kg/h]	E_{O_2} [kg/h]	E_{CO_2} [kg/h]	e_{NO_x} [g/kWh]	e_{CO} [g/kWh]	e_{O_2} [g/kWh]	e_{NO_x} [g/kWh]
650/2.96/M2	3.206	0.252	168.0	144.8	16.138	1.269	845.6	728.8
750/4.62/M2	4.981	0.340	278.1	243.9	13.903	0.949	776.3	680.9
700/2.96/M1	3.669	0.200	197.6	157.0	16.722	0.913	900.7	715.4
650/4.62/M1	3.866	0.797	204.6	208.9	12.526	2.583	663.0	676.9
750/2.96/DF	3.346	0.201	193.4	148.4	15.258	0.917	881.9	676.8
750/0.98/M1	1.679	0.171	144.7	86.9	20.953	2.128	1805.2	1084.0
650/4.62/ DF	4.231	0.594	211.8	208.2	13.456	1.888	673.8	662.1
700/0.98/M2	1.644	0.188	134.9	79.8	20.803	2.384	1706.9	1009.9
650/0.98/ DF	1.578	0.195	120.2	76.5	22.820	2.818	1738.7	1106.8

a) b) c)

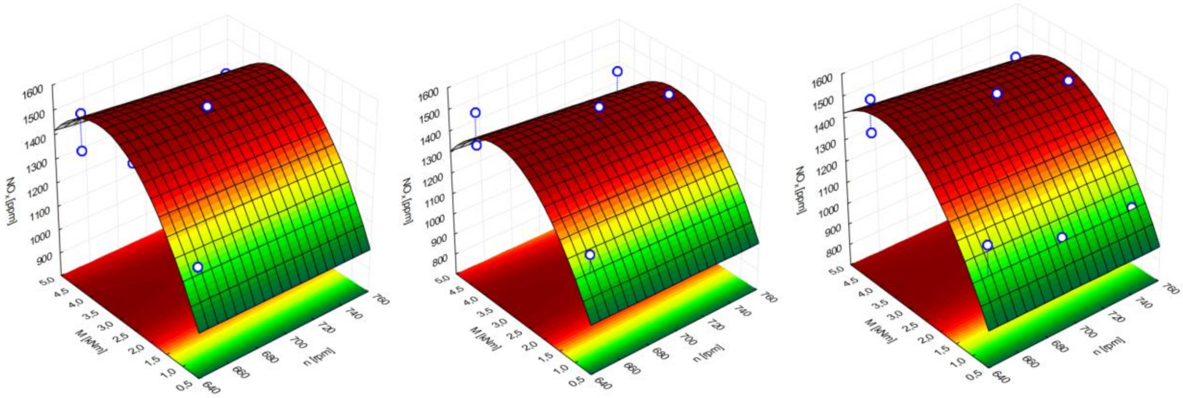

Fig. 6. Dependence of NO_x emission values depending on n and M for a) DF, b) M1, c) M2

a) b)

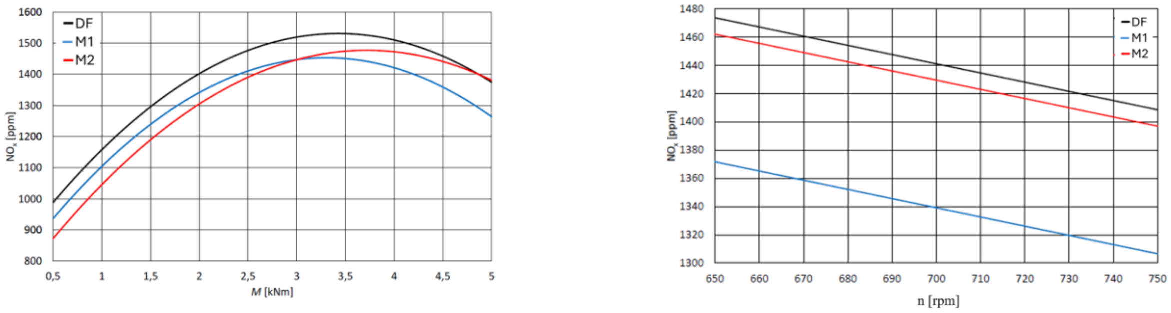

Fig. 7. Dependence of NO_x emission values at a) constant speed n = 700 rpm, b) constant torque M = 4.62 kNm depending on the fuel DF, M1, M2

loads (M > 3 kNm), fueling with mixture M1 (containing 2% water by volume) is more advantageous, also leading to a reduction in NO_x emissions of about 100 ppm (Fig. 6 a–c, Fig. 7 a–b).

It was observed that at a constant torque, NO_x emissions decrease with increasing engine speed, which a linear relationship can approximate. In higher torque ranges, the reduction in NO_x emissions results from the fact that the air excess ratio is lower, which limits the amount of oxygen available to react with nitrogen, despite higher combustion temperatures (Fig. 7 a–b).

The model fit was evaluated based on the coefficient of determination (R^2 = 0.94208) and the mean square error (MS = 15807.11), indicating a high agreement between the model and the measured data (Fig. 8).

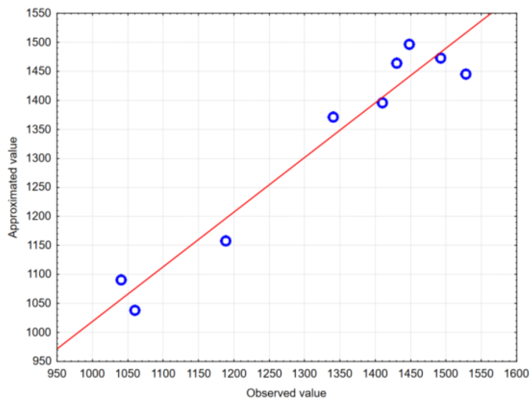

Fig. 8. Plot of observed versus approximated values for NO_x

5.4. Analysis of carbon monoxide concentrations

The analysis of carbon monoxide emission variations was carried out based on a polynomial model (Fig. 9) with a high fit to the experimental data (R^2 = 0.98454, MS = 1422.536).

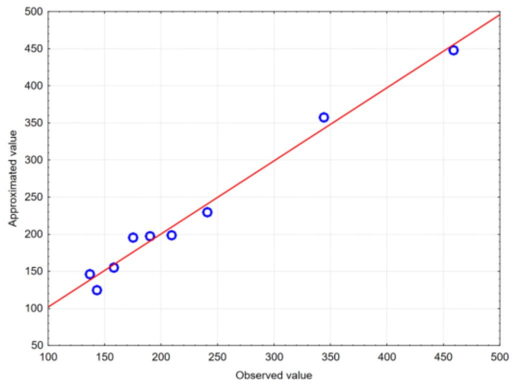

Fig. 9. Plot of observed versus approximated values for CO

The Pareto chart indicates that the quadratic relationship with torque has the greatest impact on CO emissions. Significant effects are also observed for interactions between torque and the water content in the fuel, both in linear and quadratic terms, as well as for the quadratic influence of engine speed (Fig. 10).

The research results indicate that CO emissions when fueling with diesel fuel (ON) are lower than when using the M1 blend. In the case of fuel M2, the emission pattern of

CO differs from that of ON and M1 – at low engine loads, emissions are significantly higher. In contrast, at higher loads, the CO emission level decreases.

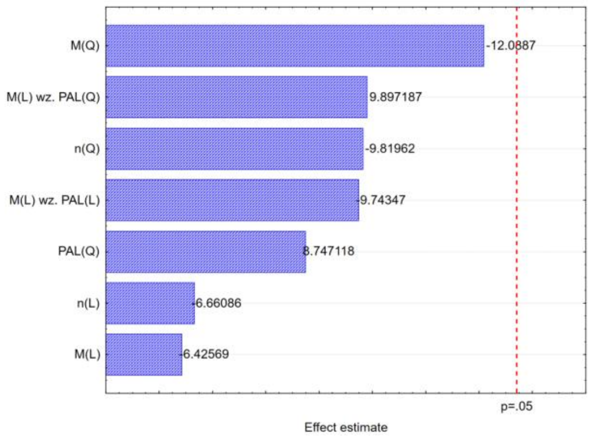

Fig. 10. Pareto charts of effect for CO

The increased CO emissions observed with M1 are attributed to a reduction in combustion temperature caused by the presence of water in the fuel. However, the mechanism behind the localized decrease in CO concentration observed at medium engine operating conditions when using the M2 blend remains unexplained (Fig. 11–12). This phenomenon may result from the catalytic effect of water, which accelerates hydrocarbon oxidation reactions.

On average, CO emissions during operation with the M1 blend are higher than the values recorded for diesel fuel (ON) by approximately 50 ppm at low loads, increasing to about 100 ppm at higher loads. In contrast, the use of fuel M2 enables a reduction in CO emissions by an average of approximately 210 ppm compared to ON, particularly at a constant engine load of 4.62 kNm (Fig. 12).

5.5. Analysis of carbon dioxide concentrations

The developed model describing the concentration of carbon dioxide (CO_2) in the exhaust gases accounts for the dependence of this compound's emissions on engine operating parameters such as rotational speed, torque, as well as on the composition of the fuel used, including the water content.

Carbon dioxide is a product of the complete and total combustion of the carbon contained in the fuel; therefore, its emissions are directly correlated with the amount of fuel burned. For this reason, the linear torque variable exerts the greatest influence on the CO_2 emission level, which was clearly confirmed by the Pareto chart analysis (Fig. 13).

This chart also indicates a significant, though less dominant, influence of higher-order interactions between engine operating parameters and the composition of the fuel mixture.

The model achieved an excellent fit to the experimental data, as confirmed by statistical indicators: a coefficient of determination R^2 of 0.99993 and a low mean square error (MS) value of 0.0003594. The high degree of fit demonstrates the model's strong predictive accuracy in the field of CO_2 emissions (Fig. 14).

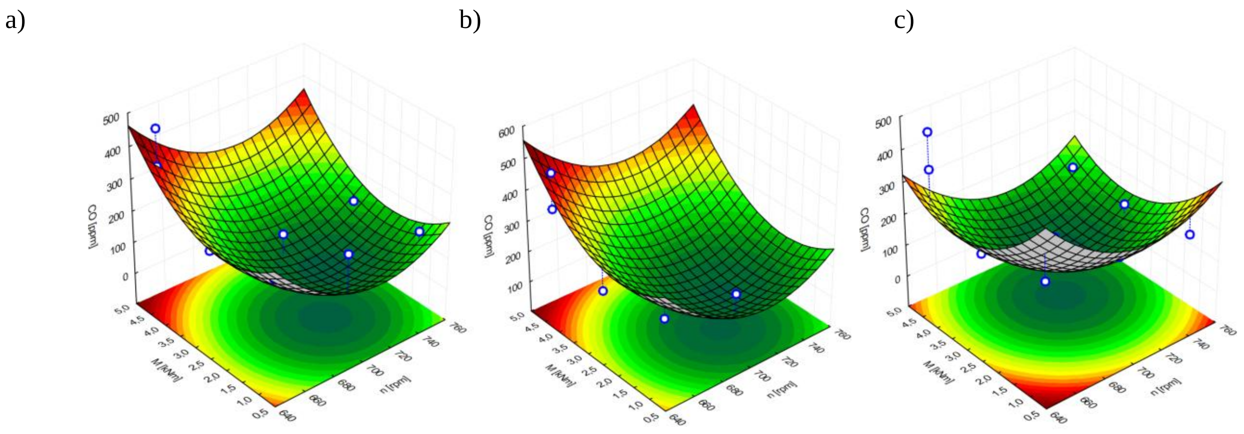

Fig. 11. Dependence of CO emission values depending on n and M for a) DF, b) M1, c) M2

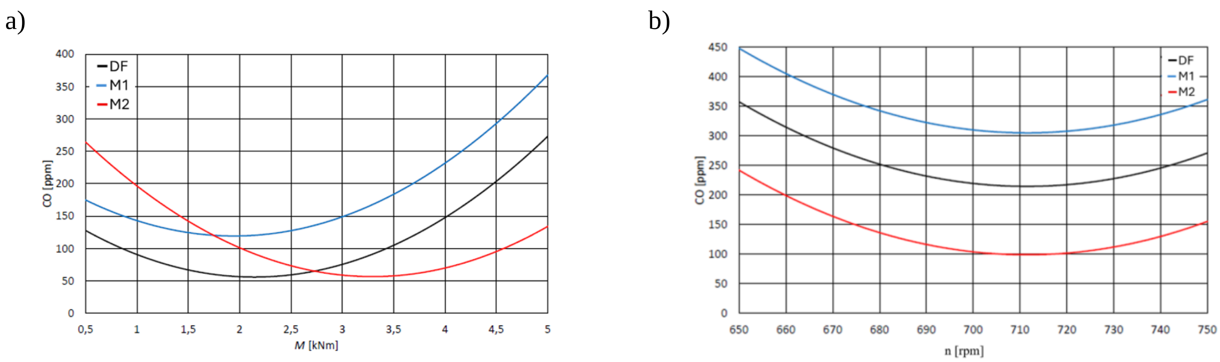

Fig. 12. Dependence of CO emission values at a) constant speed n = 700 rpm, b) constant torque M = 4.62 kNm depending on the fuel DF, M1, M2

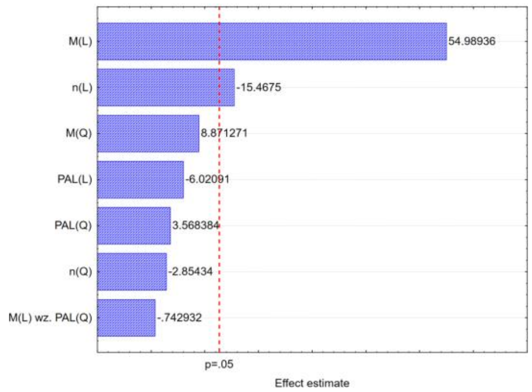

Fig. 13. Pareto charts of effect for CO_2

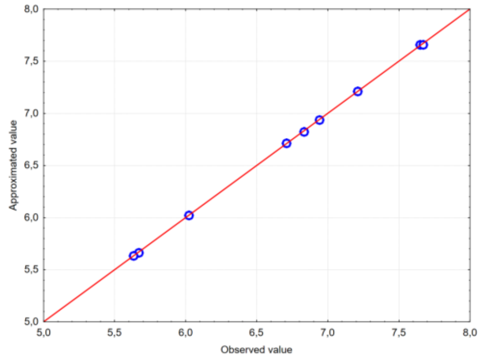

Fig. 14. Plot of observed versus approximated values for CO_2

A comparative analysis of CO_2 emissions for different fuels revealed that the concentration levels of this compound remain similar regardless of the type of fuel used (Fig. 15–16). The lowest emissions were recorded when the engine was fueled with conventional diesel fuel (DF). In contrast, the highest emissions were observed during operation with the M2 blend. However, these differences are relatively minor, suggesting that the influence of fuel composition on CO_2 emissions is limited, especially when compared to the significant variations observed in the emissions of other compounds such as NO_x or CO.

5.6. Analysis of oxide concentrations

The model describing the concentration of oxygen (O_2) in the engine exhaust gases exhibits a very high degree of agreement with the experimental results (Fig. 17), with a coefficient of determination R^2 = 0.99891 and a mean square error (MS) of 0.0094743.

The polynomial equation accounts for the influence of crankshaft rotational speed, torque, and the composition of the fuel mixture. The linear dependence on torque exerts the strongest effect on the O_2 level in the exhaust gases (Fig. 18). An increase in torque leads to a reduction in the air excess ratio (λ), resulting in greater utilization of oxygen during combustion and a decrease in its concentration in the exhaust gases.

a) b) c)

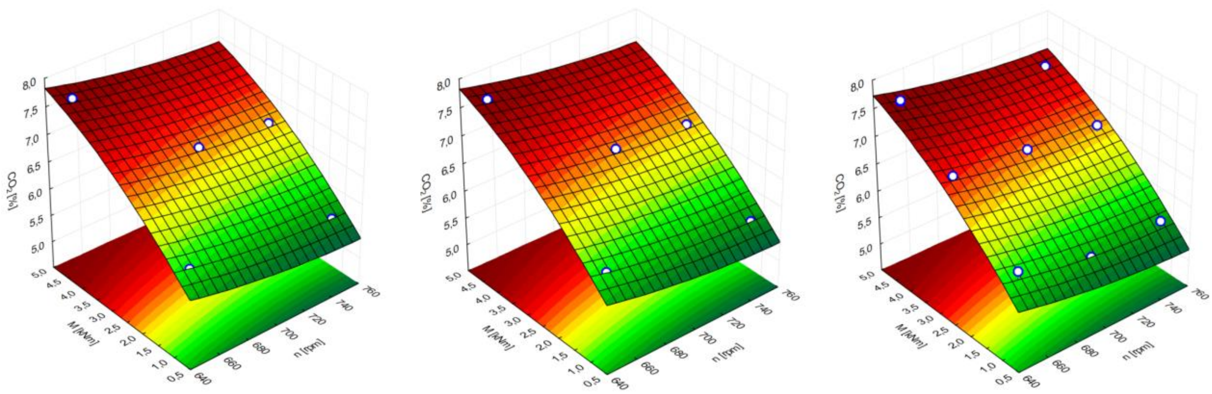

Fig. 15. Dependence of CO_2 emission values depending on n and M for a) DF, b) M1, c) M2

a) b)

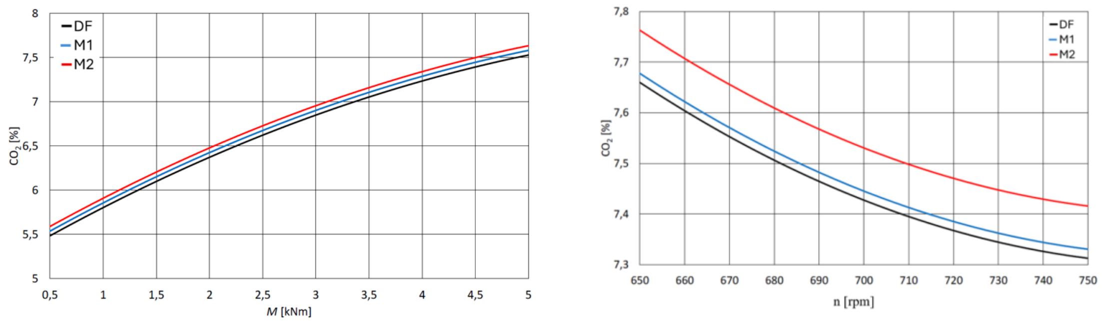

Fig. 16. Dependence of CO_2 emission values at a) constant speed n = 700 rpm, b) constant torque M = 4.62 kNm depending on the fuel DF, M1, M2

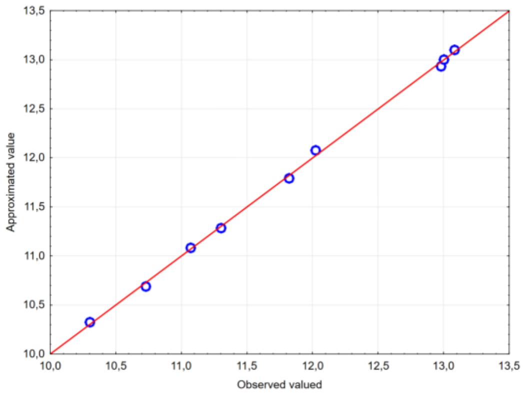

Fig. 17. Plot of observed versus approximated values for O_2

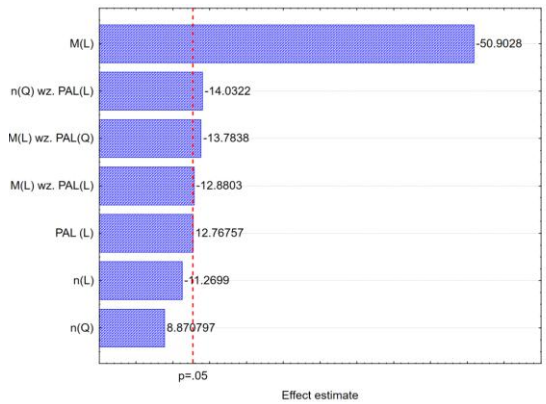

Fig. 18. Pareto charts of effect for O_2

Analyses (Fig. 19 and Fig. 20) showed that when operating on diesel fuel, the oxygen concentration decreases with increasing engine load, and this effect is more pronounced for the M1 and M2 blends. This results from the lower calorific value of butanol, which necessitates an increased fuel injection quantity into the cylinder to maintain the desired power output. The maximum O_2 concentration is observed in the range of 690–720 rpm, corresponding to the highest value of the air excess ratio.

6. Conclusion

The conducted analysis demonstrated that the use of component fuels containing butyl alcohol and water contributes to a reduction in the emissions of toxic exhaust gas constituents in marine engines. However, the nature of these changes is complex and depends on engine operating conditions.

Nitrogen oxides (NO_x) emissions were generally lower when using component fuels compared to conventional diesel fuel. The greatest reduction in NO_x emissions, reaching up to 7.5%, was achieved when operating on the M2 blend under lower torque conditions. However, at higher engine loads, the use of the M1 blend proved more advantageous. A key factor in reducing NO_x emissions is the introduction of water into the fuel blend, which lowers the maximum combustion temperature, thereby limiting the formation of NO_x, as its emission increases exponentially with rising temperatures in the combustion chamber.

In the case of carbon monoxide (CO) emissions, the results were less unequivocal. When the engine was fueled with M1, an increase in CO emissions was observed compared to operation on diesel fuel. For low engine loads, using the M2 blend resulted in higher CO emissions than with diesel; however, at higher torque values, emissions decreased and were lower than during operation on diesel. This may be related to the reduction in combustion temperature caused by the presence of water in the blend or to a potential catalytic effect of water, accelerating hydrocarbon oxidation reactions.

The concentration of oxygen (O_2) in the exhaust gases decreased with increasing engine torque, which is associated with a reduction in the air excess ratio due to the need for higher fuel injection quantities. However, for the M1 and M2 blends, the oxygen content in the exhaust gases at higher loads was higher than that observed when operating on diesel fuel. This is most likely related to the presence of oxygen in the butanol molecule, which participates in the combustion process, partially substituting for oxygen from the intake air.

Carbon dioxide (CO_2) emissions were similar across all tested fuels, which results from the fact that CO_2 is the final product of complete carbon combustion. The differences in

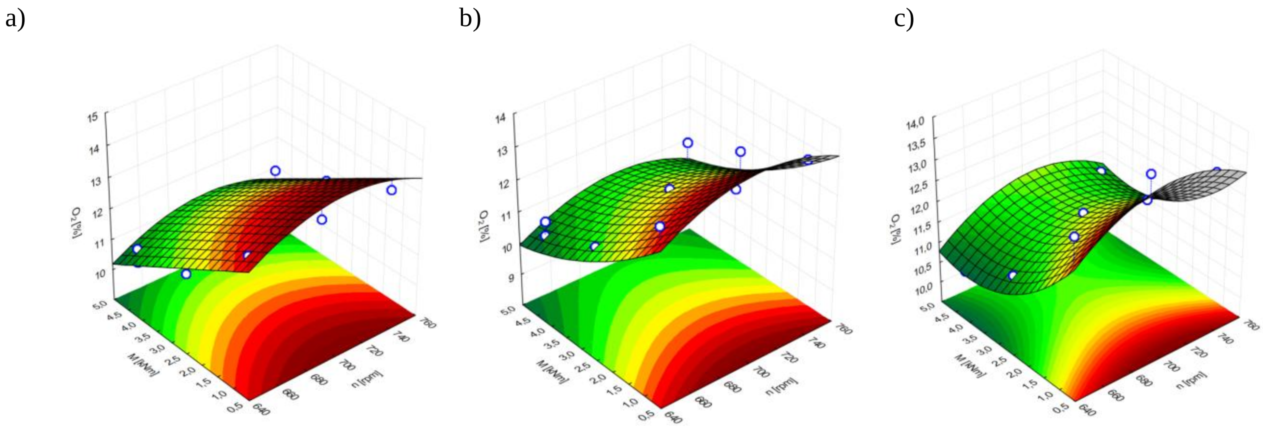

Fig. 19. Dependence of O_2 emission values depending on n and M for a) DF, b) M1, c) M2

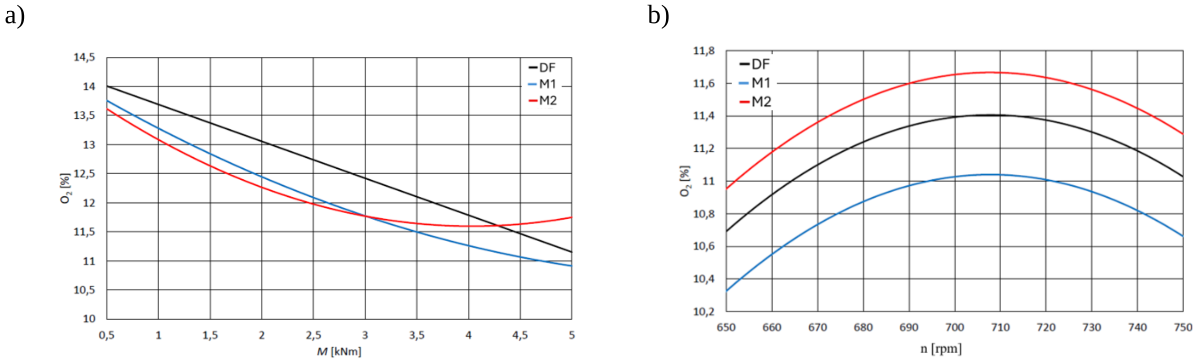

Fig. 20. Dependence of O_2 emission values at a) constant speed n = 700 rpm, b) constant torque M = 4.62 kNm depending on the fuel DF, M1, M2

emissions between fuels were minor, confirming that to obtain a given amount of energy, a comparable amount of carbon must be burned, regardless of the type of fuel used.

In conclusion, the research results suggest that the use of component fuels, particularly those containing water and butyl alcohol, may contribute to reducing emissions of harmful exhaust compounds while maintaining comparable engine operating parameters. However, due to the complexity of combustion processes and the influence of numerous operational variables, further experiments are necessary to elucidate the mechanisms underlying these phenomena fully and to ensure optimal operating conditions for marine engines while meeting environmental protection requirements.

Nomenclature

EPA	U.S. Environmental Protection Agency
EtOh	ethyl alcohol
FAMEs	fatty acid methyl esters
HC	hydrocarbons
IMO	International Maritime Organization
MARPOL	International Convention for the Prevention of Pollution from Ships
MS	mean square error
PAHs	polycyclic aromatic hydrocarbons
PM	particulate matter
R^2	coefficient of determination
REE	rapeseed oil methyl esters

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Prof. Ryszard Zadrąg, DSc., DEng. – Faculty of Mechanical and Electrical Engineering, Polish Naval Academy, Poland.
e-mail: *r.zadrag@amw.gdynia.pl*

Paweł Socik, MEng. – Faculty of Mechanical and Electrical Engineering, Polish Naval Academy, Poland.
e-mail: *p.socik@amw.gdynia.pl*

Prof. Marcin Zacharewicz, DSc., DEng. – Faculty of Mechanical and Electrical Engineering, Polish Naval Academy, Poland.
e-mail: *m.zacharewicz@amw.gdynia.pl*

Artur Bogdanowicz, DEng. – Faculty of Mechanical and Electrical Engineering, Polish Naval Academy, Poland.
e-mail: *a.bogdanowicz@amw.gdynia.pl*

Norbert Sigiel, DEng. – Faculty of Navigation and Naval Weapons, Polish Naval Academy, Poland.
e-mail: *n.sigiel@amw.gdynia.pl*