

Article

Research of the Effectiveness of Selected Methods of Reducing Toxic Exhaust Emissions of Marine Diesel Engines

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Abstract: The article's applications are very important, as it is only a dozen or so years since the current issues of protection of the atmosphere against emissions of toxic compounds from ships. The issue was discussed against the background of binding legal norms, including rules introduced by the IMO (International Maritime Organization) in the context of the MARPOL Convention (International Convention for the Prevention of Pollution from Ships), Annex VI, with the main goal to significantly strengthen the emission limits in light of technological improvements. Taking these standards into account, effective methods should be implemented to reduce toxic compounds' emissions to the atmosphere, including nitrogen oxides NO_x and carbon dioxide CO_2 . The purpose of the article was, based on the results of our own research, to indicate the impact of the effectiveness of selected methods on reducing the level of nitrogen oxides and carbon dioxide emitted by the marine engine. The laboratory tests were carried out with the use of the one-cylinder two stroke, crosshead supercharged diesel engine. Methods of reducing their emissions in the study were adopted, including supplying the engine with fuel mixtures of marine diesel oil (MDO) and rapeseed oil ester (RME)-(MDO/RME mixtures) and changing the fuel injection parameters and the advance angles of fuel injection. The supply of the engine during the tests and the mixtures of marine diesel oil (MDO) and rape oil esters (RMEs) caused a clear drop in emissions of nitrogen oxides and carbon dioxide, particularly for a higher engine load, as has been shown. The decrease of the injection advance angle unambiguously makes the NO_x content in exhaust gas lower.

Keywords: ships diesel engines; exhaust gas emission; fuel mixtures; rapeseed oil methyl ester; marine diesel oil; fuel injection parameters

1. Introduction

Global warming, i.e., in the last approximately 50 years, the observed gradual increase in the average temperature at the Earth's surface, is a phenomenon caused by the influence of humans on the intensification of the greenhouse effect.

It is estimated that over the last century, the average temperature at the Earth's surface has increased by around $0.74\text{ }^\circ\text{C}$ (± 0.18) [1], but 2018 IPCC (Intergovernmental Panel on Climate Change) data indicate a 1.5 degree increase in this temperature [2].

The industrial revolution is most often associated with global warming. The official position of the IPCC (Intergovernmental Panel on Climate Change—the Intergovernmental Panel on Climate Change) says that “most of the observed increase in global average temperatures since the mid-twentieth century is probably due to the increase in anthropogenic greenhouse gas concentrations” [3].

Greenhouse gases are commonly deemed inter alia as water vapor, carbon dioxide, methane, chlorofluorocarbons, nitrous oxide, and halons. Of these, marine engine exhaust gas includes more than

5% water vapor and approximately 5% carbon dioxide, which is an integral product of the combustion of fossil fuels. Since the amount of carbon dioxide emitted is proportional to the quantities of unburnt fuel, it can be concluded that the piston engine commonly used as a source of ship propulsion is the friendliest for the atmosphere from the known conventional solutions. This is influenced by the efficiency of the reciprocating engines, which is the highest among all heat engines [4,5].

It is estimated that the total amount of carbon dioxide that is emitted into the atmosphere by the burning of fuels is about 26,583 million tons per year. Only approximately 2% of this figure represents CO₂ from ship engines used for the propulsion of ships at ~521 million tons per year. These data are shown in Figure 1. Despite these favorable data for maritime transport, the aim is now to drastically reduce the negative impact of maritime transport on atmospheric pollution.

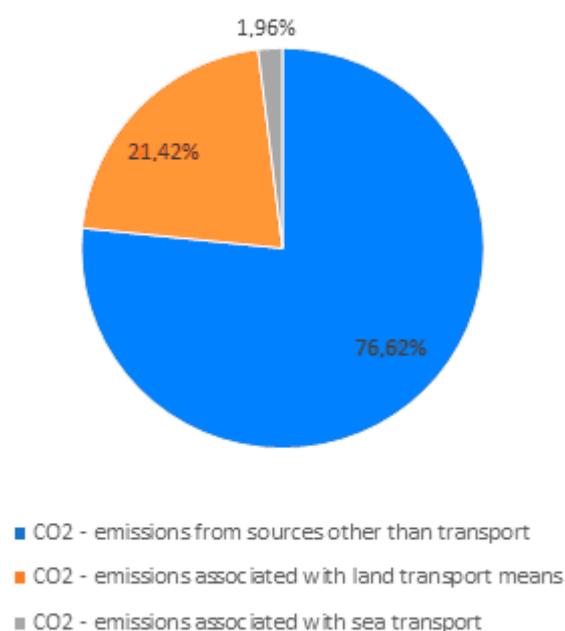


Figure 1. Percentage share of global emissions of CO₂ by source of origin (own compilation according to [1]).

Atmosphere protection against pollution from sea vessels is one of the most important areas of human ecological activity, which has its own history as well as some achievements. The most crucial ones include 73/78 MARPOL Convention (International Convention for the Prevention of Pollution from Ships) referring to prevention against marine environmental pollution, and later amendments to the Convention with Annex VI dealing with reducing the emission of nitric oxides and sulphur oxides into the atmosphere by sea vessel engines. It also prohibits deliberate emissions of ozone-depleting substances, regulates ship-board incineration, and the emissions of volatile organic compounds from tankers (MARPOL Annex VI). Annex VI entry came into force on May 2005. Already, in July 2005, the Marine Environmental Protection Committee (MEPC) agreed to revise MARPOL Annex VI, with the main goal of significantly strengthening the emission limits in light of technological improvements. In October 2008, MEPC adopted the revised Annex VI and the associated NO_x Technical Code 2008, which entered into force on 1 July 2010. They concerned a progressive reduction globally in emissions of oxides of nitrogen (NO_x), sulphur oxides (SO_x), and particulate matter (PM), and a reduction of the emission in emission control areas (ECAs). ECAs are the Baltic Sea, North Sea, and North American and United States Caribbean Sea.

2. Exhaust Emission by Marine Diesel Engine

Exhaust emitted by marine diesel engines contains a number of combustion products that are noxious to the environment. The composition of these gases depends on the content of working liquids

delivered to the engine, that is on the air, fuel, and lubricating oil (see Figure 2), and the combustion process. Exhaust gases emitted from marine diesel engines comprise nitrogen (N₂), oxygen (O₂), carbon dioxide (CO₂) and water vapor (H₂O), and pollutants, including nitrogen oxides (NO_x), sulphur oxides (SO_x), carbon monoxide (CO), hydrocarbons (HC), and particulate matter (PM).

Specific emission of the toxic components (kg/kWh) of exhaust gases is a basic coefficient of atmospheric pollution. Typical analysis of the exhaust gases from a modern low-speed two-stroke marine diesel engine is shown in Figure 2.

2.1. Control of NO_x Emissions

Nitrogen oxides (NO_x) are formed from nitrogen and oxygen at high temperatures of combustion in the cylinder. NO_x emissions are considered carcinogenic compounds and contribute to the formation of photochemical smog and acid rain.

A global approach to the control of NO_x emissions has been undertaken by the IMO through Annex VI to MARPOL 73/78.

Annex VI applies to engines with power over 130 kW installed on new ships built after 1 January 2000 (the date the keel was laid) and pre-built engines that are subject to significant technical changes.

The starting NO_x emission level recommended by the IMO (dependent on the rotational speed of the engine crankshaft—*n*) is as follows:

- 17 g/kWh when the diesel engine *n* is less than 130 rpm;
- $45 \times n^{-0.2}$ g/kWh when $2000 > n > 130$; and
- 9.84 g/kWh when $n > 2000$ rpm.

Amendments agreed by IMO in 2008 will set progressively tighter NO_x emission standards for new engines, depending on the date of their installation (see also Table 1).

Table 1. The maximum content of NO_x by MARPOL Annex VI.

Year	The Maximum Content of NO _x in the Exhaust Gas		
	<i>n</i> < 130	130 ≤ <i>n</i> < 2000	<i>n</i> ≥ 2000
2000	17.0	$45 \times n^{-0.2}$	9.8
2011	14.4	$44 \times n^{-0.23}$	7.9
2016 *	3.4	$9 \times n^{-0.2}$	1.96

* The maximum content of NO_x in areas of special control. In areas of common border with the values of 2011.

Tier I applies to diesel engines installed on ships constructed on or after 1 January 2000 and prior to 1 January 2011, and represents the 17 g/kWh NO_x emissions standard stipulated in the original Annex VI.

Tier II covers engines installed in a ship constructed on or after 1 January 2011, and reduces the NO_x emission limit to 14.4 g/kWh.

Tier III, covering engines installed in a ship constructed on or after 1 January 2016, reduces the NO_x emissions limit to 3.4 g/kWh when the ship is operating in a designated ECA. Outside such an area, Tier II limits will apply.

Much tougher curbs on NO_x and other emissions are set by regional authorities, such as California’s Air Resources Board, and Sweden has introduced a system of differentiated ports and fairway dues, making ships with higher NO_x emissions pay higher fees than more environment-friendly tonnage of a similar size.

To show compliance, an engine has to be certified according to the NO_x technical code and delivered with an Engine International Air Pollution Prevention (EIAPP) certificate of compliance. The certification process includes NO_x measurement for the engine type concerned, stamping of components that affect NO_x formation, and a technical file, which is delivered with the engine.

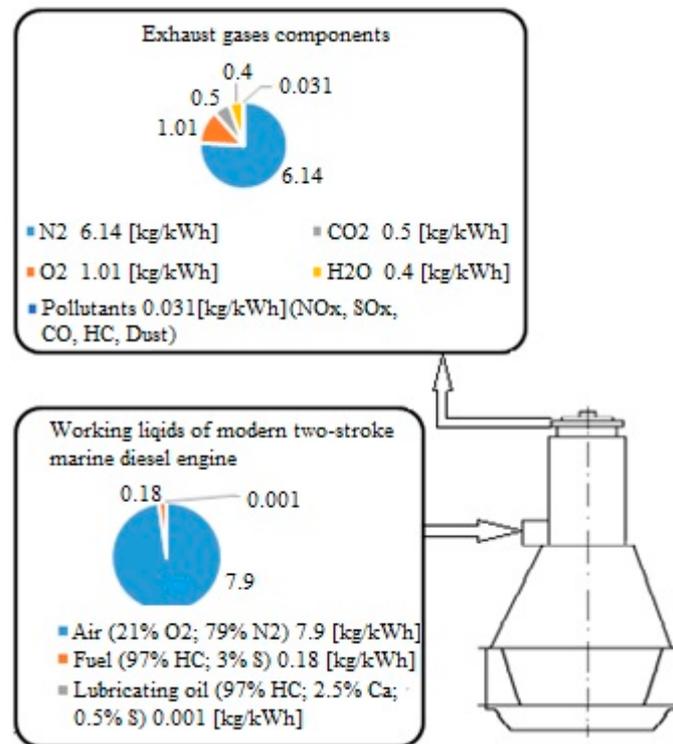


Figure 2. Exhaust gas components of a modern two-stroke marine diesel engine (based on [4]).

NO_x technical code-certified engines have a technical file, which includes the applicable survey regime, termed the onboard NO_x verification procedure. The associated parameter check method effectively stipulates the engine components and range of settings to be adopted to ensure that NO_x emissions from the given engine, under reference conditions, will be maintained within the certified value.

2.2. The Overall Amount of Global Sulphur Oxide Emissions at the Sea and in the Port Areas

Studies on sulphur pollution showed that in 1990, SO_x emissions from ships contributed around 4% to the total in Europe. In 2001, such emissions represented around 12% of the total and could rise to as high as 18%.

The simplest approach to reducing SO_x emissions is to burn bunkers with a low sulphur content. A global heavy fuel oil sulphur content cap of 4.5% and a fuel sulphur limit of 1.5% in certain designated sulphur emission control areas (SECAs), such as the Baltic Sea, North Sea, and English Channel, are currently mandated by the International Maritime Organization (IMO) to reduce SO_x pollution at the sea and in the port areas. In 2008, the IMO approved further amendments to curb SO_x emissions (see also Figure 3):

- The fuel sulphur limit applicable in emission control areas (ECA)s from 1 March 2010 would be 1% (10,000 ppm), reduced from the existing 1.5% content (15,000 ppm).
- The global fuel sulphur cap would be reduced to 3.5% (35,000 ppm), reduced from the existing 4.5% (45,000 ppm), effective from 1 January 2012.
- The fuel sulphur limit applicable in ECAs from 1 January 2015 would be 0.1% (1000 ppm).
- The global fuel sulphur cap would be reduced to 0.5% (5000 ppm) effective from 1 January 2020. Currently, all limits apply.

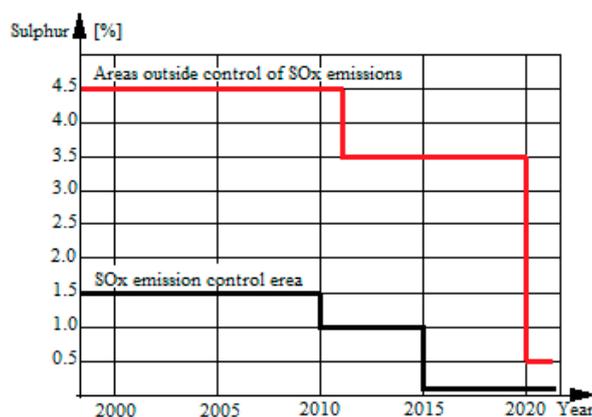


Figure 3. The maximum sulphur content of marine fuel by the MARPOL Convention (author's drawing based on the data with [6]).

2.3. Control of CO₂ Emissions

In total, 6% (0.5 kg/kWh) of the exhaust gas emission from marine diesel engines is carbon dioxide. Although it is nontoxic itself, carbon dioxide contributes to the greenhouse effect (global warming and climate change) and hence to changes in the Earth's atmosphere. This gas is an inevitable product of combustion of all fossil fuels, but emissions from diesel engines, thanks to their thermal efficiency, are the lowest of the all heat engines. A lower fuel consumption translates to reduced carbon dioxide emissions since the amount produced is directly proportional to the volume of fuel used, and therefore to the engine or plant efficiency.

International concern over the atmospheric effect of carbon dioxide has stimulated measures and plans to curb the growth of such emissions, and the marine industry must be prepared for future legislation. There are currently no mandatory regulations on carbon dioxide emissions from shipping, but they are expected. Under international agreements, such as the Kyoto Protocol and the European Union's accord on greenhouse gases, many governments are committed to substantial reductions in the total emissions of carbon dioxide.

The Conference of Parties to the International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 relating thereto, held from 15 to 26 September 1997 in conjunction with the Marine Environment Protection Committee's 40th session, adopted Conference resolution 8 on CO₂ emissions from ships. The Marine Environment Protection Committee, at its 59th session (13 to 17 July 2009), agreed to circulate the guidelines for voluntary use of the ship energy efficiency operational indicator (EEOI) as set out in the annex. This document constitutes the guidelines for the use of an energy efficiency operational indicator (EEOI) for ships. It sets out:

- What the objectives of the IMO CO₂ emissions indicator are;
- How a ship's CO₂ performance should be measured; and
- How the index could be used to promote low-emission shipping, in order to help limit the impact of shipping on global climate change.

2.4. Reduction of NO_x Emissions

Fuel brought to marine engine cylinders contains potential and chemical energy, which changes by a combustion process into the thermal energy. Analysis of the combustion process in the cylinder and the reactions that are involved in nitric oxide (NO) has identified three main sources of NO of which some are converted to nitrogen dioxide (NO₂) to give the NO_x mixture: Thermal NO, fuel source, and prompt NO. Thermal nitric oxides are produced in exhaust in temperatures higher than 1500 K. Prompt nitric oxides are produced in the flame front, in which there is deficiency of oxygen.

The range of thermal nitric oxide emissions depends on the flame temperature, partial oxygen pressure in exhaust (air excess coefficient), time of nitrogen, and oxygen particles' presence in high

temperatures. The higher the temperature in which the oxidation and concentration of oxygen take place in the reaction area, the more intensive the reaction of oxidation and the oxygen concentration that occurs. During fuel combustion in the engine cylinder, the temperature exceeds 1600 K so the conditions for nitric oxide creation are perfect.

The second group comprises nitric oxides created from nitrogen compounds included in fuel, which form nitric oxide by oxidation of combustible components, and then molecule nitrogen. The stage of nitrogen conversion from fuel into NO_x depends on the fuel type and it ranges from 20% to 80%. Over 90% of oxides of NO_x produced in internal combustion engines constitute NO. The oxidation of NO into NO_2 takes place in the engine outlet channels, with the presence of oxygen contained in the channels and in the atmosphere. The term nitric oxides comprises both compounds.

Heavy fuel oil burnt in marine engines (HFO) contains greater amounts of nitric compounds than marine diesel oil (MDO). The nitric oxide emissions are greater in the case of heavy fuel than in MDO.

The reduction of the exhaust emission of NO_x of modern marine diesel engines can be achieved through:

- Primary measures;
- Secondary measures; and
- Fuel modifications.

Primary reduction of exhaust emission takes place by influencing the fuel combustion process in the engine cylinder. The purpose of this action is to attack the problem at its source during the process of exhaust formation. In practice, in order to reduce nitric oxide emission, the following steps are taken:

- Change of air parameters;
- Change of fuel injection parameters;
- Supplying water to the cylinder; and
- Exhaust gas recirculation.

Secondary measures are necessary to apply external treatment of exhaust gases after they have left the engine cylinders. In practice, the devices available for this purpose include selective catalytic reduction (SCR)—SCR converters.

The reduction of NO_x emission through fuel modification is achieved, inter alia burning in the engine, by fuel/water emulsion. The combustion of alternative fuels, including diesel oil mixture with vegetable oils or their esters, may also be taken into account.

3. Vegetable Oils

Contemporary main diesel engines of sea-going ships are commonly supplied with heavy fuels oil (HFO). This very often also concerns auxiliary engines, especially electric generating sets. However, on many ships, the electric generating sets are still fed with marine diesel oil (MDO). Additionally, most diesel engines installed on small ships run on MDO.

Increasingly more attention is paid to alternative fuels, also called substitute, renewable, or unconventional fuels, because of the permanently increasing demand of marine diesel oil, their prices, and ecological requirements.

Unconventional fuels for supplying diesel engines are inter alia alcohol, ethanol, vegetable and mineral oils, fatty acid methyl esters, and diethyl ether [7]. In the research project planned by the author, supplying a ship with diesel engine only with a mixture of marine diesel oil (MDO) and rapeseed oil methyl ester (RME) was accounted for. It can be observed that some parameters of rape oil, their ester, and diesel oils show similar values. However, their density, kinematic viscosity, and flow temperature values differ from those of diesel oils. These data are listed in Table 2 [7].

Table 2. Comparison of some parameters of diesel oil, rape oil, and methyl ester of higher acid of rape oil (RME) [7].

Parameters	Unit	Diesel Oil	Rape Oil	Esters (RME)
Density at 15 °C	kg/m ³	820 ÷ 860	920	860 ÷ 900
Kinematic viscosity at 40 °C	mm ² /s	1.5 ÷ 4.5	30.0÷43.0	4.3 ÷ 6.3
Cetane number	–	45 ÷ 55	~51	49 ÷ 56
Gross caloric value	MJ/kg	42 ÷ 45	37.1 ÷ 37.5	37 ÷ 39
Flow temperature	°C	<–15	–6	–5 ÷ –8

As far as rape oils are concerned (interesting in the case of Poland), their density and viscosity is distinctly higher, which can make supplying diesel with them difficult; however, their positive features are practically no sulphur content and their bio-degradation ability. The results of research on the application of only vegetable oil for supplying diesel engines (mainly in the automotive industry, and not on ships) show worse cylinder filling, worse supplying, and greater lengths of injected oil jets, associated with their large viscosity and density [7]. The expected phenomena associated with supplying diesel engines with rape oil are disturbing, namely, the often occurrence of clogging sprayer nozzles in the injector, and troubles with starting engines at low ambient temperature. There is also the seizing of precise pairs of injection pumps, and great susceptibility to the formation of carbon deposits on piston heads, ring grooves, valve, and valve seats.

Due to substantial difficulties in applying rape oil only, as well as due to the limitation in using esters for running diesel engines, an alternative is to use mixtures of diesel oils and vegetable oil esters. In this way, it is expected to decrease the density and viscosity of the mixture to relative to those of a given ester. Tests on mechanical vehicles running on a mixture (20% rape oil/80% diesel oil) did not reveal any detrimental consequences [8].

Therefore, the author decided to carry out research on a marine diesel engine, to which the MDO/RME mixture containing up to 20% RME was fed.

Laboratory Tests

Object of tests. The tests were carried out with the use of the one-cylinder two stroke crosshead supercharged diesel engine, which is an element of the test stand adapted to investigations on emission exhaust gas components (Figure 4). The Wimmer MRU/2D analyzer with measuring accuracy of $\leq \pm 5\%$ and a resolution of 1 ppm was used to measure the composition of the exhaust gases.

To supply the engine during the tests in question, the marine diesel oil (MDO) and its mixtures with rape oil esters (RME) of the following proportions were prepared:

- 15% of RME in MDO; and
- 20% of RME in MDO.

The MDO had a density of 831 kg/m³ and the RME of 883 kg/m³. As a result of the mixing, the biofuel had a density of 839 kg/m³ in the first case and 840 kg/m³ in the second case.

Test program. The tests were carried out within the broad range of the engine's loading, namely: 40%, 50%, 60%, 70%, and 80% M/M_n (set torque of engine M/nominal torque of engine M_n) and for a constant rotational speed of the engine, set at 220 rpm. At a given rotational speed and successively set loads, measurements of the engine's exhaust gas content during combusting by the engine were realized: The MDO alone, and the two above specified mixtures (i.e., 15% of RME in MDO, and 20% of RME in MDO). The results obtained from the tests during the supply of the engine with the MDO alone was assumed as the reference point for determination of the influence of combustion of the MDO/RME mixtures on the engine's exhaust gas content.

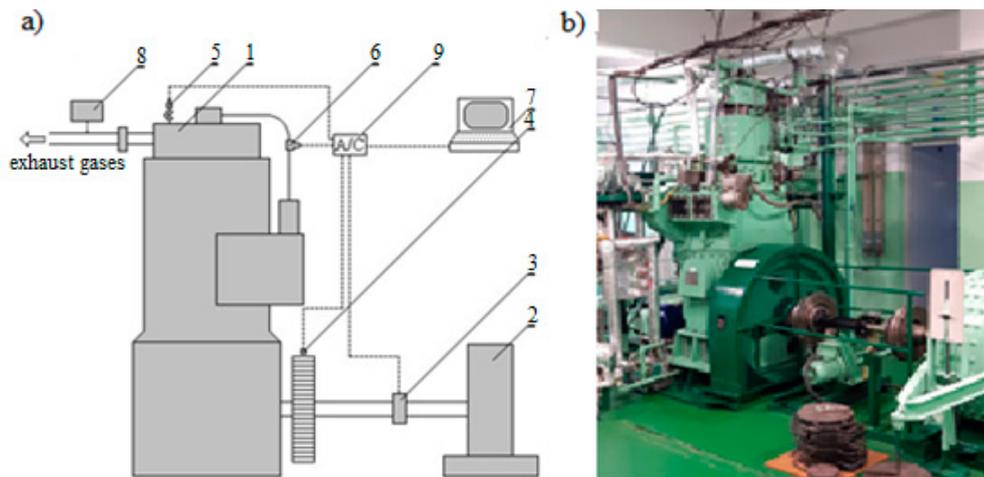


Figure 4. Test stand: (a) block diagram: 1—L-22 diesel engine, 2—water brake, 3—torsionmeter, 4—gauge for crankshaft position marking and rotational speed measuring, 5—combustion pressure transducer, 6—injection pressure transducer, 7—computer, 8—exhaust gas analyzer, 9—analog/digital converter; (b) engine L22-view.

Test results and their analysis. The selected tests results are presented in Figures 5 and 6. On the basis of the exhaust gas analysis, it can be stated that combustion of MDO with 15% addition of RME caused, on average, a drop of the NO_x content by 35% (for higher engine loads—70% and 80% M/M_n) and that during combusting of the MDO with the 20% addition of RME, the drop, on average, exceeded 57% (for higher engine loads—70% and 80% M/M_n), as shown in Figure 5.

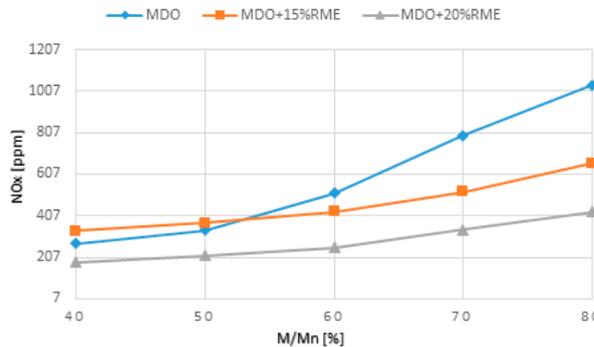


Figure 5. NO_x content in exhaust gas as a function of the engine load for different kinds of fuel at a constant rotational speed $n = 220$ rpm.

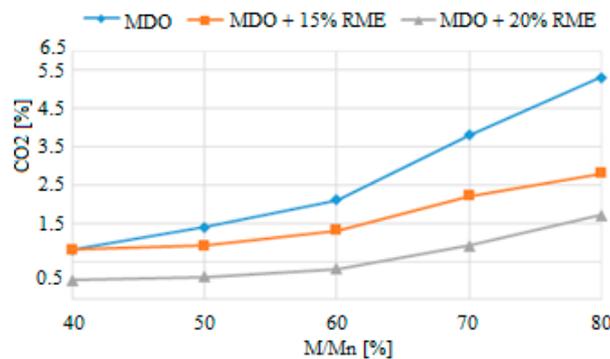


Figure 6. CO₂ content in exhaust gas as a function of the engine load for different kinds of fuel at a constant rotational speed $n = 220$ rpm.

It can also be noted that the combustion of MDO with the 15% and 20% addition of RME, especially for higher engine loads (70% and 80% M/M_n), causes a clear drop in CO_2 . This drop is exceeded by 33% in the combustion of MDO with the 15% addition of RME and exceeded by 57% in the combustion of MDO with the 20% addition of RME (Figure 6).

4. Change of Fuel Injection Parameters-Change Advance Angles of Fuel Injection

The possibility of reducing NO_x emission by changing the fuel injection parameters has been noted [9]. The fundamental parameter for an injection system is the advance angle of fuel injection. You can expect that change of the advance angle of fuel injection affects the composition of exhaust gases, including toxic component emissions. This thesis is confirmed by the research carried out by the author, described in follow section.

Laboratory Tests

Object of tests. The tests were carried out with the use of the one-cylinder two stroke crosshead supercharged diesel engine (Figure 4), which is an element of the test stand adapted to investigations on emission exhaust gas components.

To supply the engine during the tests in question, the marine diesel oil (MDO) was used and the fuel injection advance angle (injection timing) changed for three selected values:

- -13° (rated value) before the piston top dead center (TDC);
- -10° before the piston top dead center (TDC); and
- -7° before the piston top dead center (TDC).

Test program. The tests were carried out within the broad range of the engine's loading, namely: 40%, 50%, 60%, 70%, and 80% M/M_n (set torque of engine M /nominal torque of engine M_n) and for a constant rotational speed of the engine, set at 220 rpm. At the given rotational speed and successively set loads, measurements of the engine's exhaust gas content were realized for three values of the angle: -13° (rated), -10° , and -7° before the piston top dead center (TDC).

Test results and their analysis. The selected tests results are presented in Figures 7 and 8. Changes to the injection advance angle can be made by adjusting the factory settings. A decrease of the injection advance angle unambiguously makes the NO_x content in exhaust gas lower. A decrease of the injection advance angle of -13 degrees to -7 degrees unambiguously makes the NO_x content in exhaust gas lower (even more than 18%—see Figure 7). However, it should be remembered that both an advance and delay of fuel injection starting, in relation to the values recommended by the producer and set during static adjustment of the engine, influences not only the exhaust gas content but also other important operational parameters of the engine by changing the combustion process quality. Inter alia, an increase in the specific fuel consumption can be expected.

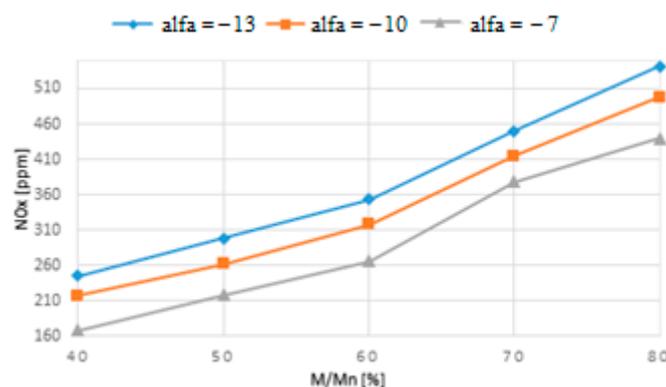


Figure 7. NO_x content in exhaust as a function of the engine load and three different advance angles of fuel injection, for a constant rotational speed $n = 220$ rpm.

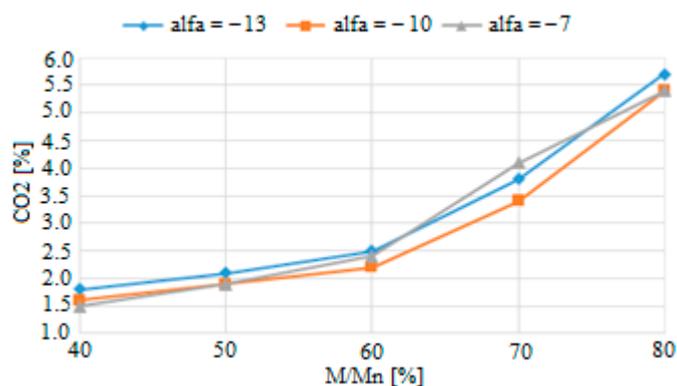


Figure 8. CO₂ content in exhaust as a function of the engine load and three different advance angles of fuel injection, for a constant rotational speed $n = 220$ rpm.

The investigations also revealed (see Figure 8) that the advance angles of fuel injection have no significant impact on the change content of carbon dioxide (CO₂) in exhaust gas.

5. Conclusions

Atmosphere protection against pollution from seagoing vessels is currently one of the most important areas of ecological activity in maritime transport. Various solutions are implemented on ships that allow for a significant reduction of toxic compounds in the exhaust gas.

Among others, fuel modifications made possible a reduction of the emission of toxic components of exhaust gases from modern marine diesel engines. The test results show that for environmental reasons, mixtures of marine diesel oil and rape oil esters (MDO)/(RME) may be supplied to the marine engines.

The supply of the engine during the tests, the mixtures of marine diesel oil (MDO) and rape oil esters (RME), caused a clear drop in emissions of nitrogen oxides and carbon dioxide, particularly for a higher engine load.

There is a possibility of reducing the emission of NO_x through changes of the fuel injection parameters. The effect of changes to the fuel injection advance angle of emission oxides of nitrogen (NO_x) and carbon dioxide (CO₂) was investigated in the test.

The decrease of the injection advance angle unambiguously makes the NO_x content in exhaust gas lower. The investigations also revealed that the advance angles of fuel injection change and they have no significant impact on the change content of carbon dioxide (CO₂) in exhaust gas.

The use of biofuels (a mixtures of marine diesel oil and rapeseed oil esters), or a reduction in the advance injection angle are the possible solutions to be used immediately, without significant investment costs.

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Conflicts of Interest: The authors declare no conflict of interest.

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