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Evaluation of Nitrogen Oxide (NO) and Particulate Matter (PM) Emissions from Waste Biodiesel Combustion

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Abstract: The results of an experimental study of nitrogen oxide (NO) and particulate matter (PM) concentrations in the exhaust gas of a compression-ignition engine used in agricultural tractors and other commercial vehicles are presented. The engine was fueled with second-generation biodiesel obtained from used frying oils (classified as waste) and first-generation biodiesel produced from rapeseed oil as well as, comparatively, diesel fuel. Tests were conducted on a dynamometer bench at a variable load and a variable engine speed. The levels of PM and NO emissions in the exhaust gas were determined. The study showed significant environmental benefits of using first- and second-generation biodiesel to power the engine due to the level of PM emissions. The PM content, when burning ester biofuel compared to diesel fuel, was reduced by 45–70% on average under the speed and load conditions implemented. As for the concentration of nitrogen oxide in the exhaust gas, no clear trend of change was shown for the biodiesel in relation to the diesel fuel. The level of NO emissions in the range of full-power characteristics was found to be lower for both tested biofuels compared to diesel fuel at lower engine speeds by an average of 7–8%, while in the range of a higher rotation speed, the NO content in the exhaust gases was higher for the tested biofuels compared to diesel oil by an average of 4–5%. The realized engine performance tests, moreover, showed an unfavorable effect of the biodiesel on the engine energy parameters. In the case of biofuels, this was by more than 4% compared to diesel fuel.

Keywords: PM; NO emissions; 1st and 2nd generation biodiesel; full load characteristic; heavy duty diesel engine; partial load characteristic of engine

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Citation: Wasilewski, J.; Krzaczek, P.; Szyszlak-Bargłowicz, J.; Zając, G.; Koniuszy, A.; Hawrot-Paw, M.; Marcinkowska, W. Evaluation of Nitrogen Oxide (NO) and Particulate Matter (PM) Emissions from Waste Biodiesel Combustion. *Energies* **2024**, *17*, 328. https://doi.org/10.3390/en17020328

Academic Editor: João Fernando Pereira Gomes

Received: 16 November 2023
Revised: 31 December 2023
Accepted: 5 January 2024
Published: 9 January 2024

1. Introduction

Due to the observed increase in the number of motor vehicles in operation in recent years and their continuous improvement, emissions of harmful products generated during vehicle operation, i.e., engine exhausts, heavy metals and particles of materials scraped from tires and road surfaces, and brake linings and clutch discs, have become a serious threat on a worldwide scale [1–3]. This problem is so important that the automotive industry is now putting environmental aspects at the top of its agenda. All major automobile corporations are implementing newer and improved, yet more complex technologies in vehicle power units. This is due to the fact that toxic emissions are directly affected by the design and operational parameters of engines [4]. However, a complete reduction in harmfulness seems impossible, so very low levels are sought. At the same time, the pressure to develop environmentally friendly vehicles with the least possible impact on the environment or with zero emissions continues unabated [5–8].

In the case of compression-ignition engines, the exhaust gas toxic components that pose the greatest challenges are NOx (nitrogen oxides) and PM (particulate matter). The processes affecting their formation of components make their elimination or reduction difficult. The main factors affecting the formation of nitrogen oxides in the combustion chamber are a high temperature and high excess air. Typically, the proportion of nitrogen in the fuel is insignificant, which does not affect the formation of NOx, while their main source is the oxidation processes of atmospheric nitrogen.

Nitrogen monoxide (II) (NO) is formed inside the engine cylinders, in the after-gas zone, based on the so-called extended Zeldovich model, which is most often used to describe its formation:

$$O + N_2 <=> NO + N$$

$$N + O_2 <=> NO + O$$

$$N + OH <=> NO + H$$

Subsequently, nitrogen oxide in the exhaust system and later in the atmosphere quickly transforms into nitrogen dioxide (NO_2). NO and NO_2 are found in motor exhausts in the greatest quantity and determine negative impacts on humans and the environment, while NOx further includes other oxides such as N_2O, N_2O_3, N_2O_4, and N_2O_5 [9–11]. Nitrogen oxides affect the nervous system, lungs, and respiratory tract. They cause weakness, dizziness, a lowered blood pressure, and, at high concentrations, even human death. In addition to their contribution to smog formation, nitrogen oxides fall as acid rain, damaging vegetation and buildings and poisoning subcutaneous waters [12].

Due to the NOx and PM emissions associated with the combustion of transportable fossil fuels, internal combustion engine power science faces the challenge of abandoning conventional pathways and adapting to the requirements of future neutrality in terms of greenhouse gas emissions and toxic exhaust components. The knowledge gained from fossil fuel combustion research can be applied and extended to study the combustion of new, non-fossil, potentially emission-free fuels, building on both theory and experimentation and using analytical techniques for monitoring and detecting pollutants [13,14].

It is estimated that in the total greenhouse gas emissions, emissions from the transportation sector account for 14.3%, with road transportation accounting for the largest share at 10.7%. In contrast, emissions from the agriculture, forestry, and land-use sectors are twice as large at 22.3%, with fuel combustion accounting for 2.2% [15].

Particulate matter (PM) is solid matter, the main component of which is soot that determines the black coloration of exhaust gases (smoke), which is a product of the incomplete combustion of fuel and engine oil. The main factors affecting its formation are excess air in the fuel mixture, the composition of the fuel, and the quality of the fuel jet injected into the combustion chamber. The characteristics of the formation of the combustible mixture cause local variations in oxygen content and the formation of oxygen deficiency, which promotes the formation of particulate matter. Attention should also be paid to the condition of the injection system, which deteriorates during engine operation and affects the quality of the combustible mixture formed.

The following PM components are distinguished [16–18]:

- Insoluble organic fraction (IOF), i.e., carbon in the form of soot and products of incomplete combustion of fuel additives and oil;
- Insoluble inorganic fraction (INSINOF), which consists of ash, sulfates, trace amounts of elements such as iron, phosphorus, calcium, chromium, etc., and mechanical impurities from the environment;
- Soluble organic fraction (SOF), i.e., organic substances absorbed on soot particles (mainly hydrocarbons formed from the incomplete combustion of fuel and oil);

- Soluble inorganic fraction (SINOF), resulting mainly from the presence of sulfur in the fuel, from which sulfuric acid is formed following combustion, and the presence of water vapor.

In the combustion chamber, the injection of cool fuel into hot air results in thermal decomposition (pyrolysis) of fuel particles and their dehydrogenation to acetylene, according to the Chakraborty and Long model:

$$C_mH_n \rightarrow \ldots \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2$$

Acetylene and other dehydrogenated hydrocarbons then undergo polymerization, cyclization, and further dehydrogenation at high temperatures, resulting in the formation of soot nuclei [16].

Particulate matter has different sizes and shapes. Typically, in the exhaust gas of a compression-ignition engine, there are small (10 to 80 nm), single elementary particles of soot in the shape of a sphere called nanoparticles and large ones (10 to 50 µm) in the form of clusters of these particles forming agglomerates or aggregates of soot (more than 100 µm) [17]. Particulate matter PM10 (particulate matter with a dimension smaller than 10 µm) and PM2.5 (particulate matter with a dimension smaller than 2.5 µm), contributing to respiratory diseases, are considered particularly dangerous to human health. In addition, some of the products of the incomplete combustion of fuel and oil absorbed on the surface of soot show carcinogenic effects [16,19,20].

Numerous studies [19,21,22] confirm that the permissible concentrations of these components in the atmospheric air of large urban agglomerations with heavy traffic are significantly exceeded. As a result, in many cities, among other things, bans are being introduced on cars with diesel engines or those meeting older emission standards entering the centers of these agglomerations.

The minimization of NOx and PM emissions in modern engines meeting current Euro VI standards is realized by the simultaneous use of EGR exhaust gas recirculation and selective catalytic reduction SCR (for NOx reduction) as well as the installation of a DPF particulate filter (for PM reduction) [9,23].

The production of fuels with refined chemical composition and properties adapted to the stringent normative requirements of modern engines also plays an important role in reducing exhaust gas toxicity. Reducing the harmfulness of exhaust gases can be achieved by improving the quality of combustion and reducing the fuel requirements of engines. Due to dwindling oil reserves and rapidly rising prices of petroleum-based fuels, efforts are being made to replace them with green energy sources, including the use of various types of biofuels, including biodiesel, to power internal combustion engines. In Poland, biodiesel, on an industrial scale, is produced by the transesterification reaction of rapeseed oil triglycerides with alcohol (usually methanol) in the presence of a catalyst (NaOH, KOH), resulting in the formation of fatty acid esters and glycerol (Figure 1). When the triglyceride contains residues of different fatty acids, a mixture of esters is obtained. In industrial production, the transesterification of rapeseed oil is usually carried out by the pressure method at a pressure of about 10 MPa and a temperature of about 240 °C [24].

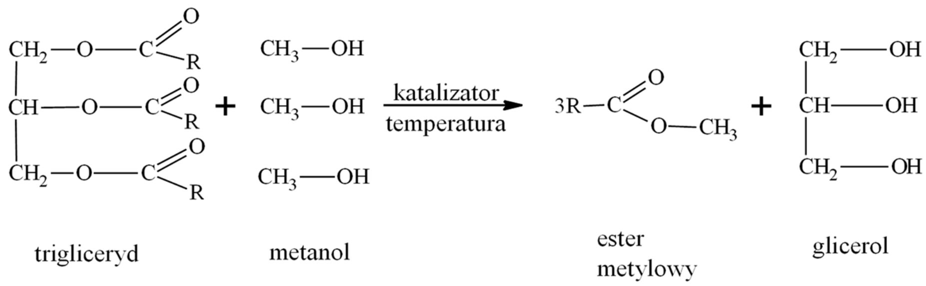

Figure 1. General scheme of the transesterification reaction [24].

Biofuel production technologies have been modified and upgraded depending on the generation of the fuel. The production of first-generation biofuels using edible feedstocks is currently being restricted so as not to create competition between biofuel production and food production [25]. In addition to various vegetable oils, waste oils and animal fats can be used to produce biodiesel [26–29]. An example of this type of second-generation biodiesel of Polish production is UCOME, which is mainly exported to energy companies in Europe. Waste oil left after food preparation is best suited for industrial purposes, usually for processing into biodiesel, which is the most efficient solution to the problem of its disposal. Biodiesel from waste cooking oil is a promising renewable source for compression-ignition engines [30].

The need to produce more and more energy results in the search for new fuel sources. Hydrogen is indicated as the main energy carrier in the future. However, producing green hydrogen from renewable energy sources still faces a great challenge [31]. Therefore, the main source of biofuels is still biomass, but it comes from sources other than edible raw materials. Such a source is, for example, lignocellulosic biomass, from which synthetic biodiesel can be obtained, among other things, by the Fischer–Tropsch process [32]. Another promising source for the production of next-generation biofuels (biodiesel, biohydrogen, and biomethane) is algae. With regard to biodiesel, the process of converting algal biomass into biofuel is best understood and described in the studies [33–35].

The utilization of waste products is one of the priorities in many areas of the economy. In the case of transportation (automotive), an important issue is the use of new-generation biofuels to power vehicle power units [30,36]. Biofuels of this type are being studied thoroughly from the ecological and operational point of view in various types of engines for different purposes. Numerous multifaceted results of biodiesel-fueled diesel engines can be found in scientific reports for mainly automotive vehicles [37,38]. Much less attention has been paid to the use of biodiesel to power commercial vehicle engines, including agricultural tractor engines. Agricultural tractors, due to the nature of their work, often operating under heavy loads, consume significant amounts of fuel [39,40]. This, in turn, results in a significant increase in the amount of emitted toxic compounds contained in the exhaust gases.

It is, therefore, reasonable to use eco-fuels, including biodiesel, in tractor engines. This paper includes the results of a study on the emissions performance of a 4.5 John Deere tractor engine, also used in trucks and as industrial stationary engines. This research is part of a broader, multi-directional study of this engine. The purpose of the research of this study was to conduct comparative, comprehensive bench tests of the engine, fueled by three types of fuel. This research used (1) second-generation UCOME biodiesel from used frying oils (categorized as waste), (2) first-generation RME biodiesel, and (3) diesel fuel (DF) as a reference fuel. Tests were carried out on a dynamometer bench in an engine dynamometer at a varying engine speed and full load (external characteristics) and at a fixed speed and varying load (load characteristics).

2. Materials and Methods

2.1. Characteristics of the Fuels Used

The following fuels were used in this study: second-generation biodiesel UCOME (used cooking oil methyl esters) and first-generation biodiesel RME (rapeseed oil methyl esters), produced by Wratislavia Biodiesel S.A., as well as the commercial diesel Efecta Diesel (DF). The biofuels met the quality standards set for biodiesel in the EN 14214 standard and for diesel in the EN 590 standard. The physical and chemical properties of the tested fuels were determined. The tests included the cetane number, density, kinematic viscosity, flash point, calorific value, and elemental composition (C, H, and N). A summary of the methods and apparatuses is shown in Table 1. The tests of fuel properties were carried out in at least 3 repetitions, from which the arithmetic mean was drawn.

Table 1. Apparatus and methods for determining selected physicochemical properties of the tested fuels.

Parameter	Method	Apparatus
Cetane number	according to ASTM D 613	Eralitic ERASPEC
Density at 15 °C	ASTM D 4052	Eralitic ERASPEC
Viscosity at 40 °C	ISO 3104	Rehotek
FAME content	according to EN 14078	Eralitic ERASPEC
Flash point	according to ASTM D 93	Eralitic ERAFlash
Carbon	-	Leco CHN 628
Hydrogen	-	Leco CHN 628
Nitrogen	-	Leco CHN 628
HHV	ISO 1928	Leco AC 600
LHV	ISO 1928	Leco AC 600

2.2. Engine Test Stand and Procedure

The tests were conducted on a four-cylinder turbocharged John Deere 4045TF285JD compression-ignition engine. The engine has a rated power of 74 kW achieved at 2400 rpm and a maximum torque of 353 Nm, corresponding to 1600 rpm. It has a combustion system with a direct high-pressure common rail fuel injection into a toroidal chamber in the piston.

Measurements were made on an engine dynamometer bench (Figure 2). On the bench, a John Deere 4045TF285JD engine was coupled to an EMX-200/6000-type electro-rotor brake with a maximum absorbed power of 200 kW. The engine speed was measured using an inductive sensor. The exhaust gas intake was from the exhaust system, downstream of the turbine. The fuel system has 3 tanks from which the engine can be supplied with the fuel of choice, and a gravimetric fuel gauge, type ATMX2400, with fuel conditioning was used to measure the amount of fuel consumed. The temperature of the fuel feeding the engine was maintained at 40 °C. The dynamometer's control room, in addition to controlling the operation of the engine-brake unit, allows for a continuous recording of the measured parameters, their visualization, and storage in computer memory.

Figure 2. Dynamometer stand for the John Deere 4045TF285JD engine testing: 1—John Deere engine, 2—engine management unit, 3—exhaust fumes outport, 4—fume temperature probes, 5—air flow meter, 6—air inlet filter, 7—eddy current engine brake.

The concentration of PM in the exhaust gas was measured using MAHA's MPM4 particle meter, while NO emissions were measured using MAHA's MGT5 five-component exhaust gas analyzer (Figure 3).

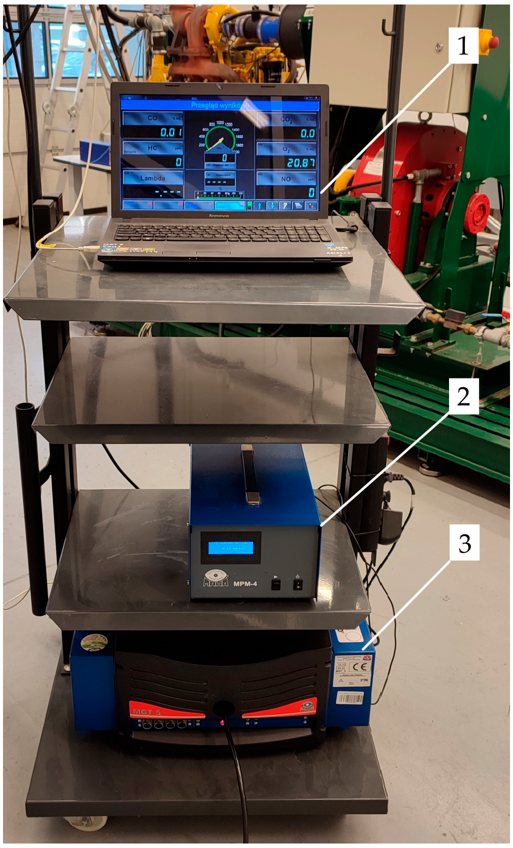

Figure 3. Measuring devices for selected components of the exhaust gas: 1—PC-data recorder, 2—MPM4, 3—MGT5.

Measurements were carried out according to the external (full power) characteristics of the engine as well as load characteristics—at two characteristic speeds: maximum torque (1600 rpm) and rated power (2400 rpm) in the full load range. When performing external engine characteristics (corresponding to the highest fuel dosage), the speed was changed in the range of 1300–2400 rpm in 100 rpm increments. On the other hand, when performing load characteristics, braking torque was changed every 25 Nm, from a “zero” load to the highest torque set on the brake (engine torque). Three repetitions were performed for each characteristic’s curve, and the obtained values of the engine parameters and emissions were averaged.

2.3. Statistical Analysis

To confirm the impact of biofuels on the emissions of the tested exhaust components compared to diesel fuel, a statistical analysis was conducted. The results were analyzed using the Statistica ver. 13 program (TIBCO Software Inc., Palo Alto, CA, USA, 2017) through an analysis of variance (ANOVA) with a significance level of $\alpha = 0.05$.

3. Results

3.1. Characteristics of the Fuels Used

Differences in the physical and chemical properties of fuels affect engine processes and lead to differences in engine performance (i.e., performance, efficiency, or emissions). Physical and chemical processes in a diesel engine—such as injection time, fuel evaporation and ignition delay—will be different when fueling the engine with biodiesel compared to petroleum diesel. In general, it can be said that the physical properties of fuels mainly affect physical processes, while chemical properties mainly affect chemical processes and the formation of emissions. The physical and chemical properties of biodiesel produced from various feedstocks compared to diesel fuel are summarized in Table 2. The results of the biofuels are in accordance with the standards in question, i.e., EN 14214.

Table 2. Selected physical and chemical properties of the tested fuels.

Parameter	Unit	UCOME	RME	DF
Cetane number	-	58	56	53
Density at 15 °C	$kg \cdot m^{-3}$	869	880	826
Viscosity at 40 °C	$mm^2 \cdot s^{-1}$	4.2	4.64	2.84
FAME content	% *w*/*w*	98.1	98.4	6.8
Flash point	°C	125	130	69
Carbon	%	77.96	78.36	86.13
Hydrogen	%	11.19	11.19	13.78
Nitrogen	%	0.153	0.137	0.094
Oxygen	%	10.69	10.58	0
HHV	$kJ \cdot kg^{-1}$	38,167	37,684	43,771
LHV	$kJ \cdot kg^{-1}$	39,347	38,864	44,951

Relating the results of the biofuels to those of the diesel fuel, it can be seen that kinematic viscosity and density are above the limits set by diesel fuel standards (EN 590). Higher values of these parameters affect the injection time, fuel atomization, and fuel evaporation, which ultimately has an indirect effect on combustion and emission formation.

Undoubtedly, an advantageous feature of biodiesel is a higher cetane number value, which will have an impact on shorter ignition delay times and combustion rates under various engine operating conditions. The shorter ignition delay of biodiesel may have a balancing effect on its impact of changing NOx emissions.

Analyzing the elemental composition (C, H, and N) of the tested fuels, differences can be observed between both biodiesel and diesel fuel types tested. Diesel contains higher amounts of carbon and hydrogen, which translates into higher heating values of such fuel. Lower carbon and hydrogen contents in biodiesel will result in different air–fuel stoichiometric ratios and lower calorific values, hence different adiabatic flame temperatures, which translates into toxic exhaust emissions.

For both biodiesels tested (UCOME and RME), a higher amount of nitrogen was observed relative to the diesel fuel. This may result in a higher amount of N_2O from the fuel forms of nitrogen for biodiesels relative to diesels. Although the contribution of non-thermal mechanisms, including fuels to emissions, is of lesser importance relative to thermal mechanisms, it should not be overlooked when analyzing emissions.

Biodiesels were found to have comparable oxygen content. The presence of oxygen in the fuel is one of the factors favoring the reduction in particulate matter in the exhaust gas and, at the same time, has a bearing on NOx emissions due to the increased amount of oxygen in the fuel mixture. The natural oxygen content of biodiesel, on the one hand, accelerates combustion processes, while on the other, it lowers its heating value. In the case of diesel fuel, research is being conducted on additives that perform an analogous function to the oxygen contained in biodiesel.

3.2. Results of Emission Tests

The measurements of NO and PM were carried out in the full-load range of the engine (highest fuel dosage), and their results are presented as a function of speed on the so-called external characteristics (Figures 4 and 5).

At rated engine operating conditions, a marked increase in exhaust nitrogen oxide emissions was recorded at low speeds of 1300 rpm and 1400 rpm (Figure 4) due to an increased nitrogen oxidation time. At speeds below 1700 rpm, lower NO emissions were recorded when the engine was fueled with bioesters, compared to being fueled with DF, by an average of 8.1% (UCOME) and 7.3% (RME). The increased NO content is caused by the higher calorific value of the fuel, which increases the combustion temperature of the fuel and, with a relatively longer engine cycle time (low speed), raises emissions of this component. On the other hand, in the higher speed range (1700–2400 rpm), the UCOME and RME biofuels proved to be less environmentally favourable. Compared to DF, the average increase in NO concentration in the exhaust gas for these two fuels was 4.8% and 4.2%, respectively. The increase in emissions is primarily due to the fuel's oxygen content.

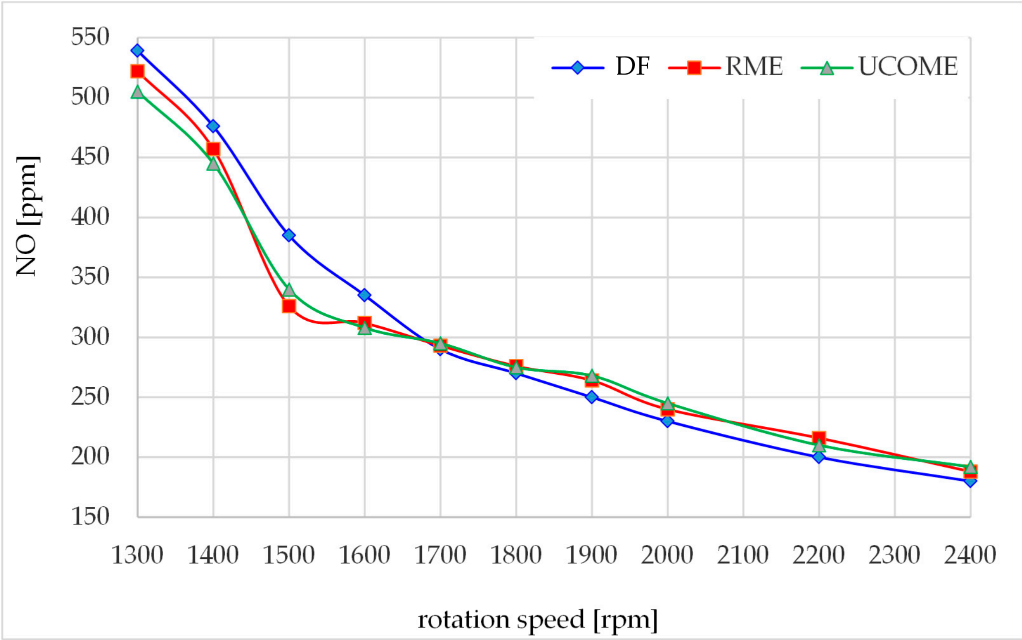

Figure 4. Effect of rotational speed on NO emissions in the exhaust of the John Deere 4045TF285JD engine.

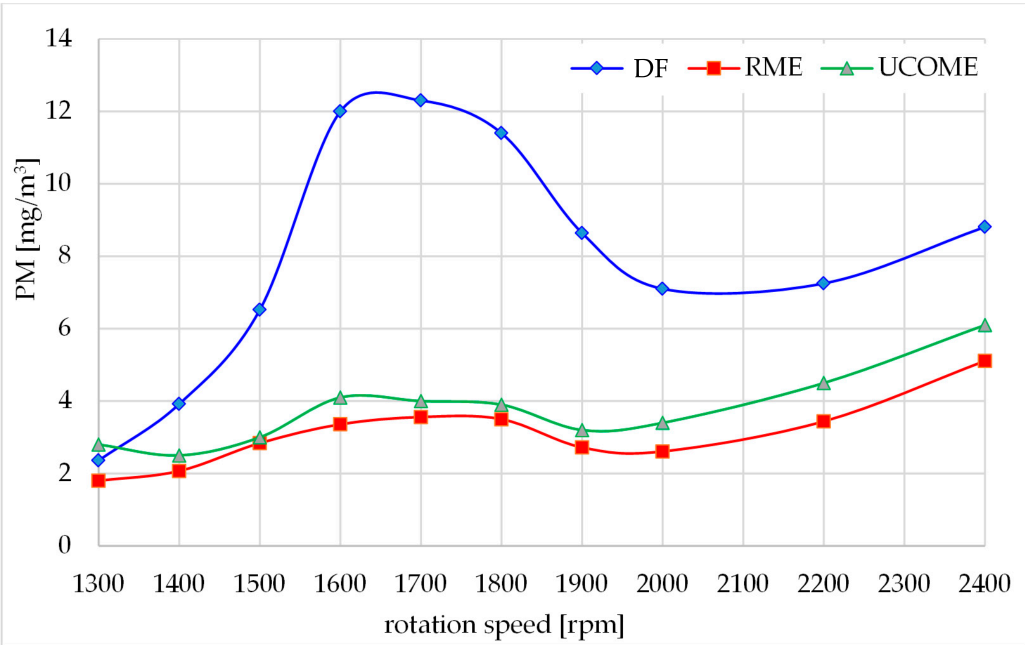

Figure 5. Effect of rotational speed on PM emissions in the exhaust of the John Deere 4045TF285JD engine.

The reasons for the change in the trend in NO emissions for DF, RME, and UCOME can be considered in many aspects. On the one hand, the chemical composition and oxygen content of biofuels influence changes in NO emission levels, and an increase in emission values could be expected. However, in the case of the tested engine, the trend reverses around the rotational speed of 1700 rpm. This is related to changes in the fuel pressure level in the fuel supply system, and the pressure values are presented in the work of Krzaczek et al. [41]. For a full engine load in the range of 1400 to 1600 rpm, the fuel pressure decreases from 90 MPa to 75 MPa and then increases linearly to 105 MPa at 2400 rpm. Local pressure reduction reduces NO emissions for all fuels, especially biofuels. Similar results for a reduced fuel injection pressure were obtained by Hunicz et al. [14]. However, an increase in the rotational speed shortens the time of the fuel combustion process and, despite the increasing fuel injection pressure, the combustion temperature decreases and, as a result, the NO emission level decreases. Therefore, the main cause of the increased NO emissions for biofuels is the over-10% share of oxygen in the composition, which translates into a several percent increase in NO emissions at higher rotational speeds at a full engine load.

For all tested engine speeds at a maximum fuel dosage, the use of biodiesel to power the test engine significantly reduced PM emissions (Figure 5). Averaged over the entire engine speed range, PM emissions were found to be lower for the UCOME and RME fuels than for DF by 45.4% and 56.6%, respectively. The crucial factor in reducing the ignition delay time is the presence of oxygen or oxidizing additives in the fuel, and for this reason, a significant reduction in PM emissions was recorded for the biodiesel. This is particularly evident in the range of maximum torque engine operation, which is often used in operating conditions.

The PM content graph in Figure 5 reveals dynamic changes in its level, particularly for the DF. As already noted, the fuel injection pressure at a full load has the lowest value for rotational speeds in the range of 1500–1800 rpm, resulting in reduced NO emissions and also longer fuel injection times. This leads to a prolonged combustion process, causing an increase in PM emissions for the tested fuels at medium rotational speeds. However, for biofuels, the changes are minimal, while for the DF, they are several-fold.

The next measurement results concerned the engine's load characteristics. Figures 6 and 7 show the waveforms of changes in the emission levels of PM and NO in the exhaust gas as a function of torque for an engine speed of 2400 rpm, while Figures 8 and 9 show the changes for 1600 rpm.

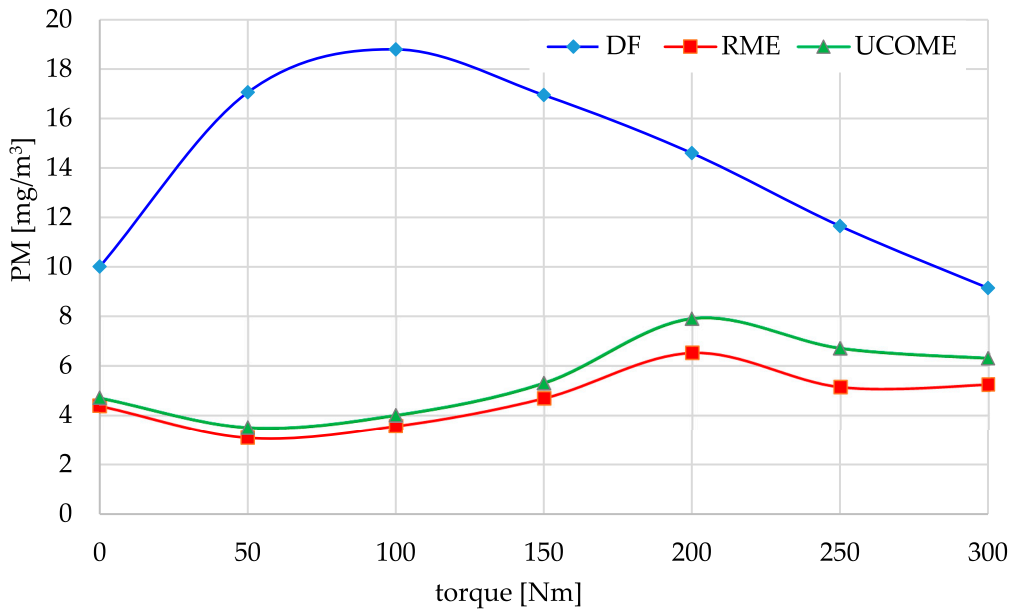

Figure 6. Effect of torque on the level of PM emissions in the exhaust gas of the John Deere 4045TF285JD engine at 2400 rpm.

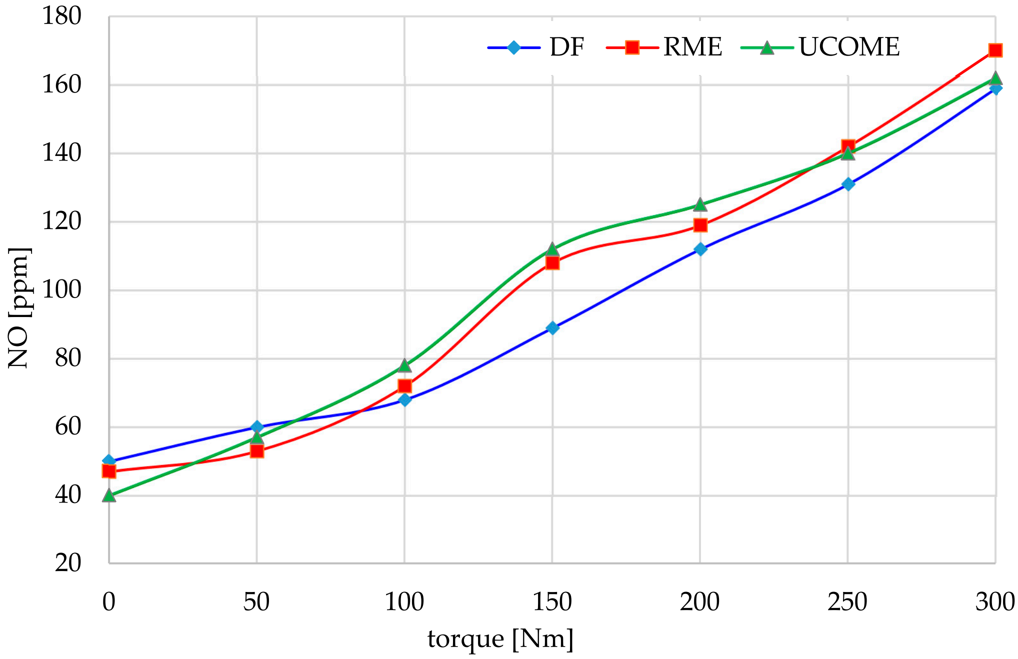

Figure 7. Effect of torque on NO emissions in the exhaust of the John Deere 4045TF285JD engine at 2400 rpm.

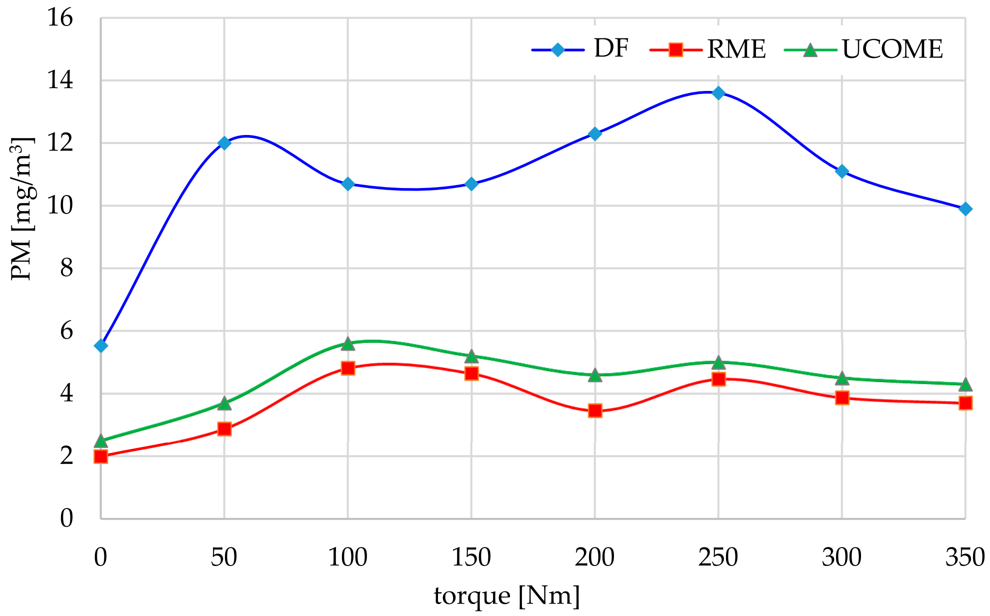

Figure 8. Effect of torque on the level of PM emissions in the exhaust of the John Deere 4045TF285JD engine at 1600 rpm.

The content of PM in biofuels changes as the fuel pressure changes. The fuel pressure increases from 90 MPa during a no-load operation to 100 MPa when the load is 100 Nm. It then decreases to 95 MPa at 200 Nm and increases again to 105 MPa above 250 Nm. An increased load leads to an increased fuel dose and slight fluctuations in the fuel injection pressure, which can increase the PM emission level up to twofold. This effect is visible in the load range between 150 and 250 Nm. In the case of DF, the PM content in the exhaust gases does not depend on the fuel pressure, and the course of the curve, depending on the load, corresponds to the course of changes in the air charging pressure through the turbocharger. Up to a load of around 100 Nm, the turbine slightly increases the boost pressure which, combined with an increased fuel dose, can almost double the PM emission level. Above 125 Nm, the boost pressure increases linearly, which increases the temperature in the combustion chamber and leads to a more effective combustion of the supplied fuel.

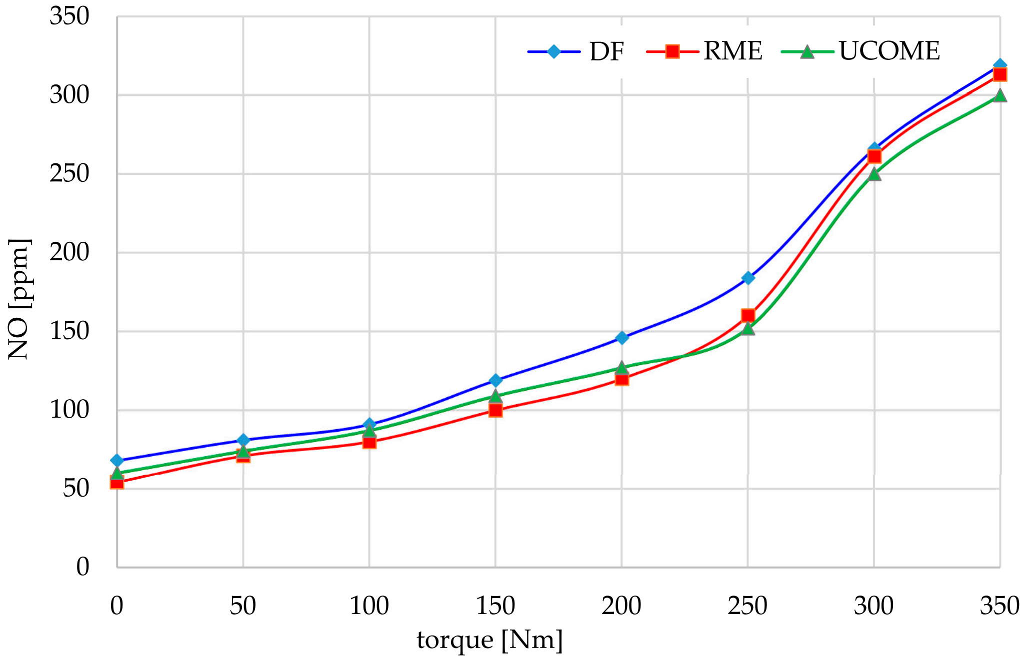

Figure 9. Effect of torque on the level of NO emissions in the exhaust gas of the John Deere 4045TF285JD engine at 1600 rpm.

As with the external characteristics, 64.8% for RME and 58.1% for UCOME at 1600 rpm were found compared to feeding the engine with diesel fuel. At feeding, the engine with biodiesel significantly reduced the concentration of particulate matter in the exhaust gas, as seen in the load characteristics (Figures 6 and 8). Averaged over the entire engine load range, the PM emissions decreased (63.6%) for RME and (57.1%) for UCOME at 2400 rpm.

The PM content curve for the DF has two peaks. This shape is due to the combination of two factors. Firstly, the engine has a turbocharger that becomes effective above 100 Nm at 1600 rpm, as mentioned in Figure 5. Secondly, the tested engine operates with the lowest values of injected fuel at 1600 rpm. At no load, the value is 85 MPa, decreasing to 50 MPa at 150 Nm, and then increasing to 75 MPa at a load of 350 Nm. Therefore, for DF, the content is twice as high at 50 Nm due to an increase in the dose of fuel fed. Then, the injected pressure is reduced by almost half, extending the injection time, which is associated with a lower temperature in the combustion chamber despite the increase in the air charging pressure. The second peak of the PM content curve for the DF appears at a load of 200 Nm, which is due to another increase in the fuel pressure and a linear increase in the boost pressure. However, for the tested biofuels, the maximum PM emission value was recorded at 100 Nm, which corresponds to the beginning of the effective operation of the turbocharger and a significantly reduced fuel injection pressure.

The measurements show that, at a speed corresponding to the engine's rated power, the concentration of NO in the exhaust gas turned out to be higher for the ester biofuel relative to the DF, by an average of 5.1% for UCOME and 4.5% for RME (Figure 7). On the other hand, at the rotational speed corresponding to maximum torque, biodiesel turned out to be more favorable from the point of view of nitrogen oxide emissions (Figure 9). For the UCOME and RME fuels, as an average over the entire engine load range, 9.4% and 11.9% decreases in NO emissions were obtained compared to running on DF, respectively.

The amount of fuel injected and the level of emissions are determined by the engine controller. At higher engine speeds above 1800 rpm (as shown in Figure 4)—which is at rated loads—there is a change in the tendency of the NO emission level. This has been confirmed by the load characteristics in Figures 7 and 9, which show the same change trends in the entire range of load changes. Biodiesel is more favorable than diesel fuel from the point of view of NO at 1600 rpm, while diesel fuel is more favorable at 2400 rpm. PM emissions are also determined by the engine controller, which selects the injected fuel dose based on the load and engine speed. However, diesel fuel has higher PM emissions (as seen in Figures 5, 6 and 8) compared to biodiesel on both full power and load characteristics.

Reports in the literature [42] confirm that the content of toxic components in the exhaust gas when biofuels are used to power internal combustion engines is inconclusive. Elevated nitrogen oxides in the exhaust gas and varying emissions of carbon dioxide and particulate matter may be a concern. However, hydrocarbon emissions are always lower when fueling with rapeseed biofuel. As the authors emphasize, powering compression-ignition engines with plant-based fuels is ecologically and economically sound. A study [43] describes similar observations. An increase or decrease in NOx emissions during biodiesel combustion was observed depending on the engine type and testing procedures. On average, NOx emissions increased by 10% when burning pure biodiesel (B100). Few authors have found a reduction in NOx emissions when burning biodiesel [44].

There are some challenges with NOx emissions from biodiesel-fueled diesel engines. Changing engine parameters, treating them with an antioxidant additive, and blending fuels can be used to reduce NOx emissions when burning biodiesel. The paper [45] proves that one effective method is to burn dual or blended fuels. Different fuels, such as gasoline, hydrogen, natural gas, and biogas, and different types of alcohols can be used to reduce the disadvantages of biodiesel [46,47]. Reductions in NOx emissions can be achieved by using most fuels in blending with biodiesel under all engine operating conditions, provided the proper injection parameters and fuel mixing ratios are maintained.

Despite the negative aspects associated with fueling internal combustion engines with biodiesel, the combustion of this biofuel has been recognized as a control technology in reducing gaseous pollutants in order to create a sustainable and healthy scenario for humans and the environment. Burning biodiesel as a transportation fuel results in a reduction in total emissions of polycyclic hydrocarbons, aromatic hydrocarbons, carbon oxides, and sulfur oxides by 67%, 80%, 48%, and 100%, respectively. Emission assessments from the literature strongly suggest that the use of biodiesel is effective in reducing pollutants, which is beneficial for balancing human impacts on the environment [48].

The environmental benefits associated with the significant reduction in particulate emissions of compression-ignition engines fueled by biodiesel are confirmed by both domestic and foreign studies. For example, the authors of [37,49,50] demonstrated an approximate 50% reduction in PM emissions for B100 biodiesel compared to DF. A similar decrease in exhaust PM concentrations (45–65%) for different engine loads was found by the authors of this publication. In their study, the authors simultaneously found an increase in NOx for B100 fuel, compared to DF, of about 10%. This was confirmed in the realized studies (4–5% increase in NO emissions at medium and high engine speeds). Another researcher [10,36] reports a reduction in PM emissions for spontaneous biodiesel in the range of 20–60%, and in the case of nitrogen oxide emissions, a range of −15% to 20% (depending on the engine tested) was found, which is confirmed by the measurement results included in this publication.

The results of the analysis of variance for PM emissions showed significant differences between the mean values (at the $\alpha = 0.05$ significance level) for the bioesters tested, compared to DF (Table 3). On the other hand, for NO emissions, in all the cases analyzed, the ANOVA results show no significant differences between the mean values.

Table 3. ANOVA results for NO (ppm) and PM (mg/m^3) emission levels due to fuel (UCOME, RME, and DF).

Type of Characteristics	Component of Exhaust	Factor	Degree of Freedom df	Totals of Squares SS	Mean Squares MS	Test Function Value F	Calculated Significance Level p
External	NO	UCOME-DF	1	259.2	259.2	0.021657	0.884639
		RME-DF	1	186.05	186.05	0.014822	0.904448
		UCOME-RME	1	6.05	6.05	0.000581	0.981037
	PM	UCOME-DF	1	91.592	91.592	15.14326	0.00107
		RME-DF	1	121.4752	121.4752	20.4497	0.000264
		UCOME-RME	1	2.106005	2.106005	2.160881	0.158827
Load	NO	UCOME-DF	1	163.3333	163.3333	0.029583	0.864677
		RME-DF	1	177.6333	177.6333	0.030021	0.863689
		UCOME-RME	1	0.3	0.3	5.46×10^{-5}	0.994155
	PM	UCOME-DF	1	405.132	405.132	58.79883	2.36×10^{-8}
		RME-DF	1	493.0069	493.0069	74.71166	2.17×10^{-9}
		UCOME-RME	1	4.30923	4.30923	2.807941	0.104932

4. Conclusions

Particulate matter and nitrogen oxides are the chemical compounds contained in exhaust gases and are extremely dangerous for the environment and living organisms. Of the toxic components of compression-ignition engine exhausts, they are emitted in the greatest quantity. Hence, various environmentally friendly measures are currently being implemented for diesel engines (similarly for gasoline engines), among which biofuels play an important role as an alternative to traditional fuels. Research into the emission performance of internal combustion engines is one of the research priorities of modern motorization, both with regard to traditional fuels and biofuels. However, it should be taken into account that the engine's emissivity and other performance indicators depend mainly on its operating conditions, design features, adopted regulations, and the degree of component wear [36,51–53].

The most significant difference in the chemical composition of biodiesel and diesel fuel is the oxygen content. Biodiesel contains 10–12% oxygen, which is favorable from the point of view of combustion in the engine. At the same time, the calorific value of biodiesel, due to its different elemental composition, is about 10% lower than that of mineral diesel. The specific consumption of biodiesel, compared to diesel, is usually more than 10% higher, which is confirmed by studies conducted under braking conditions [54,55].

Realized tests of the John Deere engine on a dynamometer bench on the level of particulate emissions (exhaust smoke) showed a very favorable impact of biodiesel on the environment. The relative PM reduction of the engine fueled by UCOME and RME, compared to DF, was 45–70%. Differences between averaged nitrogen oxide emissions at a variable speed (external characteristics) and at a variable load on the load characteristics (taking into account, in addition, other speeds in the range of 1300–2400 rpm) for the tested bioesters in relation to DF range from −12% to +5%. Positive values were related to the realization of the measurements of NO concentration in the exhaust gas at engine speeds above 1800 rpm. The realized engine performance tests, moreover, showed an unfavorable effect of biodiesel on the engine energy parameters. In the case of the biofuels UCOME and RME, this was by more than 4% compared to DF.

An increase in the share of new second-generation biofuels in the fuel sector would be welcome, produced from non-food products, preferably residues of various origins and wastes, for example, from frying oils (UCOME bioester tested), wood waste (lignocellulose), biodiesel, bioethanol, and biogas, the application of which will require testing in real facilities.

Author Contributions: Conceptualization, J.W., J.S.-B. and G.Z.; methodology, J.W., P.K. and G.Z.; validation, J.S.-B., A.K., M.H.-P. and W.M.; formal analysis, J.W.; investigation, J.W., P.K., J.S.-B. and G.Z.; resources, J.W., P.K. and W.M.; data curation, P.K.; writing—original draft preparation, J.W., J.S.-B. and G.Z.; writing—review and editing, P.K., A.K., M.H.-P. and W.M.; visualization, J.W. and P.K.; supervision, G.Z.; project administration, J.W.; funding acquisition, G.Z. All authors have read and agreed to the published version of the manuscript.

Funding: The work was carried out as part of a team project no. TKA/S/9/2023 financed by the Ministry of Education and Science as part of a grant for maintaining research potential awarded to the Faculty of Production Engineering, University of Life Sciences in Lublin.

Data Availability Statement: Data are contained within the article.

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

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