Ultralow Sulfur Diesel and Rapeseed Methyl Ester Fuel Impact on Performance, Emitted Regulated, Unregulated, and Nanoparticle Pollutants

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ABSTRACT: The operation of engines using rapeseed methyl ester (RME) and ultralow sulfur diesel (ULSD) was tested for the combustion properties, emitted regulated, unregulated exhaust pollutants, and the size of nanoparticles. The combustion analysis showed higher apparent heat release rate and shorter ignition delay period during RME combustion than during ULSD combustion. The ULSD engine has a combustion chamber maximum pressure relatively higher than that of RME. This study showed that the heat release rate of ULSD is always higher than that of RME while more fuel consumption occurred from the combustion of biodiesel in comparison with diesel. When the engine is running on RME, HC and NOx formation increased at high loads up to 15% and 13%, respectively; meanwhile, CO concentrations reduced by 30.9% for the same conditions. Most of the particulate matter (PM) emitted from a diesel engine has a particle size from 5 to 100 nm, while the particle size from ULSD ranged from 5 to 40 nm. Overloading the engine caused a decrease in the sizes of emitted PM for both fuels. The smoke number for RME was less than that for ULSD by 33.9% at high loads. For high engine load, the cumulative concentration number for the nucleation mode decreased, while it increased for the accumulation mode. Furthermore, measurements of formaldehyde, ethane, methane, acetylene, ethylene, propylene, and isocyanic acid emissions showed the presence of these harmful substances at very low concentrations (8 ppm) for both fuels.

1. INTRODUCTION

Due to the steady increase in population around the world, the rise in the standard of living, and the total dependence on transportation vehicles mostly powered by fossil fuels, the world’s fossil fuel reserves are experiencing a sharp decline. Diesel (a derivative of petroleum fuels) can be considered the most widely used in the world in the operation of vehicles, trains, ships, and electric power plants.1 The International Energy Agency (IEA) expected that all kinds of global energy would escalate by 50% from 2005 to 2030, with the dominance of fossil fuels completely on the global energy market.2 This huge dependence on diesel in all sectors of industrial, agricultural, and transportation sectors, which makes it the most influential fuel in the global economy, came as a result of the high reliability, durability, and high efficiency of diesel engines. What confuses this picture is that a large and substantial portion of greenhouse gases is emitted from diesel engine exhaust.3 Diesel engines emit harmful gases that affect the health and environment such as CO and CO<sub>2</sub>, NO<sub>x</sub>, HC, and smoke, which are called regulated emissions. In addition, there are other types of carcinogenic and dangerous gases such as acetaldehyde, acetylene, methane, ethylene, and propylene that are called unregulated emissions. The unregulated contaminants are very harmful to health and sometimes even deadly.4,5 Diesel combustion in compression ignition (CI) engines emits a complex mixture of gaseous emissions in addition to flammable nanoscale particles such as PM1 and PM2.5. Regular pollutants include NO<sub>x</sub>, SO<sub>2</sub>, HC, CO, and CO<sub>2</sub>. As for the particulate matter (PM), it is composed of organic carbon and elementary carbon.6,7 Generally, it can be considered that diesel engine exhaust pollutants have serious negative public health consequences as it reduces visibility and
Table 1. Some Recent Studies Used Biodiesel Addition to Diesel from the Literature

| ref. no. | biodiesel origin | engine used | operation conditions | brake thermal eff | bsfc | NOx | CO | HC | PM | unregulated emissions |
|---------|------------------|-------------|----------------------|-------------------|------|-----|-----|-----|----|----------------------|
| 36      | pine oil         | SC, water cooled DI diesel engine (Kirloskar AV1) | constant engine speed (15 rpm) variable loads (20, 40, 60, 80, and 100%) | 1.3% less than diesel | 6.2% less than diesel | 13.1% more than diesel | 7.5% less than diesel | 21% more than diesel | 35.5% more than diesel | nil |
| 37      | 1st generation (coconut, palm, rapeseed, soybean), 2nd generation (cottonseed, Jatropha curcas, jojoba, karanja), and 3rd generation (fish oil, spirulina, waste cooking oil, animal fats) feedstocks | diesel engine with a rated power of 3.5 kW at 1500 rpm | three compression ratios (16.5, 17.5, and 18.5:1) and variable loads (25, 50, 75, and 100%) | 0.63% less than diesel | 4% more than diesel | 39.6% | 13.1% | 21% | 35.5% | nil |
| 38      | fatty acid methyl esters | 4-cylinder diesel engine-type 1.6 HDI | varying biodiesel portions in the blend by 10, 30, and 50% | 0.78% more than diesel | 8% more than diesel | 3.29% | 10.4% | nil | 65.6% | nil |
| 39      | rice bran oil and karanja oil | single-cylinder, 4-stroke, naturally aspirated, DI diesel engine | diesel (D), hydrogen-enriched diesel, hydrogen-enriched 10 and 20% rice bran biodiesel, and hydrogen-enriched 10 and 20% karanja biodiesel blend | 2.5% less than diesel | 2.9% less than diesel | 6–13% | 4–38% | 6–14% | nil | nil |
| 40      | waste cooking oil | 4-cylinder, 4-stroke, water-cooled, 1.461-L, turbocharged CI engine | fixed engine speed 1750 rpm and variable loads (20, 40, 60, and 80 Nm); hydrogen added by 10, 20, 30, and 40 rpm | 11.1% less than diesel | 2.22% more than diesel | 4.27% | 42.7% | nil | 65.6% | nil |
| 41      | rapeseed oil + distilled tire pyrolytic oil | medium-duty compression-ignition engine manufactured by Andorza-Mot Poland | single cylinder, 4-stroke air-cooled diesel-powered Kirloskar engine (model: TAF-1) | 1.2% less than diesel | 17.5% more than diesel | 27.6% more than diesel | 78.57% more than diesel | 35% less than diesel | nil | nil |
| 42      | Chlorella emersonii methyl ester (CEME) blended with diesel at 10%, 20%, 30%, 40%, and 100% | single cylinder, 4-stroke, naturally aspirated, air-cooled, 4-stroke, single-cylinder vertical, air-cooled, diesel engine | constant speed 1500 rpm | 7.7% less than diesel | 7.4% more than diesel | 13.6% less than diesel | 8% more than diesel | 16.6% less than diesel | 20.54% more than diesel | toluene: 55% less than diesel; acetaldheyde: 8% more than diesel; formaldehyde: 45% more than diesel |
| 43      | rapeseed oil methyl ester and rapeseed oil ethyl ester | 4-stroke Yanmar diesel engine TF70V-E | variable speeds: 1000, 2000, and 3000 rpm | 11.11% less than diesel | 26.3% more than diesel | 13.47% | nil | nil | nil | nil |
| 44      | methyl oleate (MO) to palm oil methyl ester (PME) | single-cylinder direct-injection Yanmar model L48N diesel engine | part load conditions (50%) constant speed 3000 rpm | 4.9% less than diesel | 21.04% more than diesel | 78.3% more than diesel | 68.4% more than diesel | nil | nil | nil |
| 45      | waste cooking oil + ethanol/octanol | single-cylinder, vertical, 4-stroke, air-cooled, DI 170 F CI diesel engine | constant speed 1500 rpm and variable loads (20, 40, 60, and 80 Nm); hydrogen added by 10, 20, 30, and 40 rpm | 23.77% less than diesel | 5.45% more than diesel | 8.5% less than diesel | 12.7% less than diesel | nil | nil | nil |
| 46      | less than diesel | DL 4-cylinder, Puma diesel engine | variable IT conditions (before and after TDC), 1500 rpm, and two BMEP | 7.5% more than diesel | 21% less than diesel | 31% less than diesel | 23% less than diesel | nil | nil | nil |
| 47      | preheated Vateria indica methyl ester (VIME) | 4-stroke, single-cylinder TV1 Kirloskar diesel engine | blends (B0, B30, B50, and B100) with variable loads (20, 40, 60, 80, and 100%) | 7.44% more than diesel | 26.73% less than diesel | 21.62% less than diesel | 28.08% less than diesel | 42.7% less than diesel | 17.3% less than diesel | nil |
| ref. no. | biodiesel origin | engine used | operation conditions | brake thermal eff | bsfc | NOx | CO | HC | PM | unregulated emissions |
|---------|------------------|-------------|----------------------|------------------|------|-----|----|----|----|-----------------------|
| 47      | Chlamydomonas alga biodiesel | 4-cylinder OM 924 diesel engine | fixed injection timing 4° bTDC and fixed injection quantity | 5.58% more than diesel | 0.28% less than diesel | 67% less than diesel | 42% less than diesel | nil |
| 48      | biodiesel + ethanol + n-pentanol | single-cylinder diesel engine with a common rail fuel injection system, which is 4-valve, four-stroke, and water-cooled | | 30.9 less than diesel | 40.8% less than diesel | 48% less than diesel | | nil |
| 49      | Chlorella protothecoides biomass and rapeseed oil | single cylinder, water-cooled compression-ignition diesel engine (Kirloskar AV1) | | 3.4 less than diesel | 5% less than diesel | 3.3% less than diesel | 27.2% less than diesel | nil |
| 50      | rapeseed oil–methanol–iso-butanol blends | 4-cylinder turbocharged Zetor 1204 diesel engine | diesel/rapeseed oil/methanol/iso-butanol 60/30/5/5, 50/30/10/10, and 50/10/20/20 | 5.5 less more than diesel | 9.8% more than diesel | 21.9% more than diesel | 41.9% 5.2% less than diesel | 4% less than diesel |
| 51      | rapeseed methyl ester (RME)-based biodiesel and rapeseed oil (RO), blended with diesel (D) and isopropanol (P) | 4-cylinder turbocharged direct injection diesel engine | 7 different blends prepared and tested | 4% less than diesel | 1% more than diesel | 11% more than diesel | 5% more than diesel | 30% more than diesel |
| 52      | waste cooking oil | 2-cylinder, water-cooled, Simpoms S217 diesel engine | variable loads (25, 50, 75, and 100%), IT = 24° bTDC | 9.7% more than diesel | 25% more than diesel | 13.46% more than diesel | 30% more than diesel | 17% less than diesel |
| 53      | waste cooking oil | 4-cylinder, common-rail diesel | the ESC (European Stationary Cycle) used in analyzing the fuel blend impact on the exhaust constituents | 1.57% more than diesel | 11.02% more than diesel | 3.7% more than diesel | 33.9% 5.79% less than diesel | 53.8% less than diesel |
| 54      | olive mill wastewater (OMWW) | single-cylinder DI LISTER-PETTER diesel engine | IT = 13° bTDC, 1500 rpm, variable loads (25, 50, 75, and 100%) | 1.2% more than diesel | 14% more than diesel | 16.5% more than diesel | 26% less than diesel | 26% more than diesel |
| 55      | waste cooking oil and diglyme | 4-cylinder DI Isuzu 4HF1 diesel engine | 2400 rpm, 5-engine loads, and oxygen concentrations of 2, 4, 6, 8, and 10% | 1.5% more than diesel | 9.5% more than diesel | 41.6% 4% less than diesel | 5.79% 44.7% less than diesel | nil |
| 56      | waste tires pyrolysis oil (TPO) and neat palm biodiesel | turbocharged DI Renault Kangoo K9K 700 diesel engine | engine speed from 1000 to 3500 rpm and full load | 3.3% more than diesel | 4% less than diesel | 41.6% 4% less than diesel | 5.79% 20.2% less than diesel | nil |
| 57      | V. indica methyl ester (VIME) | single-cylinder, TV1 Kirloskar DI diesel engine | | 1.6% more than diesel | 16.2% more than diesel | 16.2% more than diesel | 34.4% 16.5% less than diesel | nil |
| 58      | partially hydrogenated biodiesel (PHB)–ethanol–diesel ternary blend | turbocharged, 4-cylinder common rail diesel engine | various loads and 1800 rpm | 4.7% more than diesel | 100% more than diesel | 45.45 62.5% more than diesel | 60.8% 60.8% less than diesel | 30.8% less than diesel |

HCHO emissions: 77.79% more than diesel; butadiene (C4H6): 47.1% more than diesel; 1,3-butadiene: 15.97% more than diesel; propane: 85.36% more than diesel; ethane: 63.15% more than diesel; methane (CH4): 109.1% more than diesel; formaldehyde: 25% more than diesel; acetaldehyde: 47.1% more than diesel; AHC: 31.8% less than diesel; C2H4: 37.31% more than diesel; C2H2: 63.15% more than diesel; SO2: 28% less than diesel; HCHO: 50% more than diesel; H2O: 28% less than diesel; C2H6: 29.41% less than diesel; AHC: 31.8% less than diesel.
Table 1. continued

| ref. no. | biodiesel origin | engine used | operation conditions | brake thermal eff | bsfc | NOx | CO | HC | PM | unregulated emissions |
|----------|------------------|-------------|----------------------|-------------------|------|-----|----|----|----|-----------------------|
| 59       | cottonseed and palm oil biodiesels | single-cylinder, 4-stroke, and the natural aspiration diesel engine | variable engine speed from 1400 to 2400 rpm; 100% engine load | 9.5% less than diesel | 10.4% more than diesel | 26.5% more than diesel | 18.9% less than diesel | 29.04% less than diesel | 26.05% less than diesel |  |
| 60       | C. pyrenoidosa microalgae biodiesel (CP20D80) | single-cylinder, water-cooled light commercial CI engine | PIT (pilot injection timing) of 20° aTDC and 15° aTDC and maximum load condition | 3.7% more than diesel | 2.7% less than diesel | 37.5% more than diesel | 65.2% less than diesel | 67.25% less than diesel | 67.8% less than diesel |  |
| 61       | coconut, sunflower, and palm oils | single-cylinder, water-cooled DI diesel engine | 9 blends tested at constant speed and variable load | 0.52% less than diesel | 5.3% more than diesel | 95% less than diesel | 23.5% less than diesel | 4.5% less than diesel |  |
| 62       | diethyl ether (DEE) | 3-cylinder, water-cooled, DI tractor diesel engine | 1500 rpm and variable engine loads | 33.3% less than diesel | 33.3% less than diesel |  |
| 63       | 85% light hydrocarbon (LHC)-diesel blends | six-cylinder (Z6170ZLCZ-19) diesel engine | 1000 rpm and variable loads (50, 75, and 100%) | 38.09% less than diesel | 17.6% less than diesel | 80% more than diesel | n-pentane (n-C5H12): 150% more than diesel; n-octane (n-C8H18): 170% more than diesel; isobutene (iso-C4H8): 58.8% more than diesel; formic acid (HCOOH): 50% more than diesel; formaldehyde (HCHO): 92.85% more than diesel |  |
| 64       | coconut oil-diesel fuel blends | 4-cylinder, turbocharged diesel engine | variable loads (25, 50, 75, and 100%); variable speed (1600, 2350, 3100, and 3850 rpm) | 0.84% less than diesel | 2.44% more than diesel | 11.93% less than diesel | 12.9% less than diesel | 14.79% less than diesel | nil |
causes acid rain in addition to its major role in global climate change.\(^8\,^9\) The rate of emission of any of the abovementioned pollutants depends on many overlapping variables and the sampling conditions. The most important of these variables are engine type, combustion chamber type,\(^10\) injection method and injection angle, engine operating method,\(^11\) and fuel type in addition to the after-treatment method used.\(^12\) Many countries around the world have set strict standards on emissions of exhaust gases from diesel engines. The manufacturers of these engines have also tended to develop advanced technologies for controlling engine emissions. The global research trend in the study of diesel engines works in two basic directions, namely, to reduce both specific fuel consumption (SFC) and exhaust gas pollutants to meet the standards imposed by the United States of America and the European Union.

New ignition methods are among the many options presented in this direction, and HCCI\(^13\),\(^14\) PPCI,\(^15\),\(^16\) and LTC engines have emerged.\(^17\),\(^18\) Several researchers have also added small proportions of variable types of nanoadditives to the diesel fuel in order to improve combustion characteristics and reduce pollutants.\(^19\),\(^20\) Some important studies mixed diesel fuel with water to form an emulsion that takes advantage of hydrogen and aqueous oxygen atoms in the combustion.\(^21\),\(^22\) Since the nineties of the last century until today, studies are continuing to add many types of biofuels to diesel because this fuel is produced from natural sources as it is an oxygenator that contains in its chemical composition oxygen that improves the combustion process inside the combustion chamber.\(^23\),\(^24\)

Among biofuel types, biodiesel is a very promising renewable fuel. Biodiesels can feed diesel engines without any engine modifications.\(^25\),\(^26\) Biodiesels consist of long chain fatty acid monoalkyl esters that are derived from animal fats, vegetable oils, and yellow grease. Biodiesel is sulfur-free, renewable, non-toxic, high-oxygen, and biodegradable. It has an energy density comparable to that of fossil diesel. The cetane number is less in biodiesel properties than that of diesel fuel, but it is rather close and has a high percentage of oxygen in its chemical composition.\(^27\),\(^28\) Against this beautiful picture, biodiesel is characterized by high viscosity, high molecular weight, and low volatility, and these properties cause several problems such as high sedimentation rate in the combustion chamber that causes the injector to close and stick to the piston ring.\(^29\) Moreover, diesel—biodiesel mixtures are considered unsuitable for use in cold weathers due to phase separation, which results in equipping the engine with a heterogeneous mixture of fuel.\(^30\) In general, replacing diesel with biodiesel can contribute to significant reduction in carbon monoxide, sulfur dioxide, volatile organic compounds, hydrocarbons, and PM emitted. However, most experimental studies confirm that the levels of NO\(_x\) emissions increase.\(^31\)\(^–\)\(^33\) The switch to biofuels produced from agricultural crops can be seen as a threat to global food security. Hence, most researchers in this field have adopted the use of biofuels that come from waste cooking oil from restaurants and home kitchens, but these sources are not permanent and are not a continuous supply.\(^34\) Biodiesel produced from animal fats such as inedible beef, duck fat, fish fat, and yellow fats as waste from manufacturing processes can be considered as a permanent source for preparing the raw materials for biodiesel at lower cost.\(^35\)

Table 1 lists some recent studies that investigated the addition of many types of biofuels to diesel and the resulting effect on engine performance and emissions.

In diesel engines, the internal combustion is characterized by the controlled mixing of air—fuel inside the engine cylinders. Diesel engines emit high levels of NO\(_x\) and smoke.\(^36\)\(^–\)\(^39\) The bulk of the soot is formed during the combustion period, which is controlled by mixing. In the late combustion stage, most of the soot formed is oxidized. As for NO\(_x\) it forms at high temperatures in the flame front. Exhaust gas recycling (EGR) technology is considered one of the most effective methods of reducing NO\(_x\) concentrations by reducing the flame temperature. Studies have proven that an increase in EGR rates causes a rise in PM concentrations due to a decrease in oxygen concentration in the combustion chamber, which causes disruption of soot oxidation. From here, it was found that the oxygen present in the biodiesel will solve part of this dilemma and reduce the PM concentrations, although it will cause a limited rise in the NO\(_x\) concentrations. Working with a high engine injection pressure will reduce PM concentrations, but NO\(_x\) levels will increase. Finding a way to reduce both NO\(_x\) and PM levels to fulfill stringent emission legislations can be considered a complex and difficult task.\(^40\),\(^41\)

The researchers examined several options in diesel engines to solve this issue. Moniru et al.\(^42\) added palm and Jatropha oils to diesel at rates of 10% and 20% and found that fuel consumption increased by 7.96% to 10.15%, respectively. The study showed that adding 10% Jatropha to diesel caused smoke opacity to decrease by 31.09% compared to diesel. Chaichan et al.\(^43\) studied the possibility of utilizing hydrogen entering into the combustion chamber through the intake manifold with the use of diesel—biodiesel and the recycling of cold and hot exhaust gas. The addition of hydrogen raised the temperatures inside the combustion chamber that increased the NO\(_x\) levels in the exhaust gas, while the use of EGR at high levels caused a decrease in the brake thermal efficiency. The researcher found the possibility of reducing NO\(_x\) levels by adopting the percentages of hydrogen and EGR at a specific additive. Additionally, the used technique caused a decrease in PM levels but increased engine noise.

Some researchers have adopted the multiple injection method of diesel—biodiesel mixtures to achieve low NO\(_x\) and PM levels. For example, Naresh Kumar et al.\(^44\) used an 80% diesel—20% palm oil methyl ester blend with a multiple fuel injection engine running. The injection was divided into 10%, 20%, and 30%, with two injection angles of 33\(^\circ\) bTDC and 23\(^\circ\) bTDC. The researchers claimed superior performance while NO\(_x\) levels increased by 7.19% compared to pure diesel. Karthic et al.\(^45\) added Syzygium cumini oil in various proportions (30%, 70%, and 100%) to diesel fuel and studied the effect of changing the engine injection timing (21\(^\circ\), 23\(^\circ\), and 25\(^\circ\) CA bTDC) and the injection pressure (200, 220, 240, and 260 bar) on the engine’s performance and contaminants. They concluded that the engine performance was significantly enhanced by advancing the injection timing by 2\(^\circ\) CA bTDC and raising the fuel injection pressure to 240 bar. B30 (70% diesel—30% biodiesel blend) gave the best engine performance under these operating conditions. Also, the levels of CO and HC were reduced by 15.9% and 46.15%, respectively. Engine operation at advanced injection timing and high fuel injection pressure caused reduction in the smoke level by about 28.7%. However, under these operating conditions, NO\(_x\) levels were increased.
Ashok et al.\textsuperscript{72} used a pilot injection of 10% and injection pressures of 400, 500, and 600 bar to operate an engine (type CRDI) fueled with biodiesel produced from natural lemon peel oil that had a low viscosity. The researchers also increased the pilot injection rate to 20% and 30% at a constant injection pressure of 600 bar. The last case studied was when 10% exhaust gas recirculating (EGR) was introduced at a pilot injection of 30%. The study concluded that the fuel—air mixing is better at high injection pressures, resulting in an increase in the bsfc. The fuel consumption was reduced while NO\textsubscript{X} concentrations were increased by 13.6% at engine operation with high combustion rates during the ignition-lag period. The study recommended adding approximately 20% or 30% EGR to the combustion chamber to reduce NO\textsubscript{X} levels.

Heywood\textsuperscript{73} studied the effect of adding antioxidants such as aromatic amines (DPPD, PPD) and phenols (BHT, BHA) on the NO\textsubscript{X} and smoke levels emitted from an engine powered by diesel—biodiesel (produced from sunflower) blends. Compared to diesel fuel, the engine operation with the studied blends caused a slight increase in bsfc but enhanced the brake thermal efficiency. The addition of PPD caused a decrease of 52% in NO\textsubscript{X} concentrations compared to the other antioxidants.

As shown in the above literature survey and Table 1, for most of the studies, measuring the emitted unregulated pollutants has been neglected, despite the fact that these pollutants are the most toxic and dangerous to public health. The reason may be due to the difficulty of measuring them or considering their concentrations to be very small compared to pollutants such as CO, HC, and NO\textsubscript{X}. However, these small values, when produced by millions of operating engines, will have very serious toxic effects and must be treated as the case of the regulated pollutants. Therefore, in this study, a high-speed direct injection diesel engine (HSDI) fueled with ultralow sulfur diesel and rapeseed biodiesel (RME) blends is used. To reduce the NO\textsubscript{X} and PM together, the tests were conducted under constant engine speed conditions (1500 rpm) and variable loads (four loads). A constant fuel injection pressure (800 bar) and injection timing (9° BTDC) were also used. The study aims to investigate the impact of the above engine operating parameters on the levels of regulated, unregulated, and nanoparticle emissions of the engine. The study will show conclusively that biodiesel reduces some of the regulated pollutants, but it increases the unregulated ones compared to the diesel. Therefore, serious consideration must be given to setting limits to unregulated pollutants to ensure the safety of public health and the environment.

### 2. MATERIALS AND METHODS

#### 2.1. Test Fuels

The diesel fuel used in the study is an ultralow sulfur diesel (ULSD) fuel manufactured by the Shell Company. Also, pure rapeseed methyl ester (RME) produced by the Shell Company in the UK, which is famous for the cultivation of rapeseed, was used. The production of biodiesel from rapeseed is a mature technology, but the production costs are high and are twice the price of non-taxable diesel fuel. Perhaps the bulk of the price is due to the fact that only 41% of the dry biomass weight is oil. Table 2 lists the used fuels’ properties, which were supplied by the manufacturing companies.

Table 2 shows that the number of carbon atoms in biodiesel is more than its counterparts in diesel while the cetane number is relatively higher and also the viscosity and density are much higher than the case of the diesel used. The height of the last two traits has a negative effect on the injection process as it requires higher pressures, but in this study, the used engine has a high injection pressure (800 bar), which means that these two properties will not affect the injection process. However, they will have an effect on the process of evaporation and mixing with air. Biodiesel contains 10.84% oxygen in its composition. This amount will help improve combustion and reduce pollutants. Low-sulfur diesel fuel contains 46 mg/kg oxygen, which is a low quantity, and it will limit the formation of sulfur oxides that poison catalysts. Also, a higher decrease in sulfur will reduce the formation of particulate matter. The calorific value of the biodiesel is significantly lower than the calorific value of diesel. The lower calorific value means that more biodiesel is consumed by the engine when compared with diesel to produce specific work at the same load and speed. It can be said that this property is one of the disadvantages of using biodiesel in internal combustion engines, which all types of biofuels from all feedstocks have in common.\textsuperscript{40,42,45,52,59}

#### 2.2. Test Engine

Figure 1 shows a schematic diagram of the experimental setup used in the recent study while Figure 1b shows a photo of this setup. A naturally aspirated diesel engine type Ford Duratorq (Puma) is used in the tests. This engine consists of four cylinders with a volume of 2.0 L, and each cylinder contains four valves. A Schenck eddy current dynamometer is attached to the engine’ flywheel. Table 3 illustrates the basic engine’s features.

The combustion chamber pressure is measured during operation employing a pressure transducer (type Kistler) installed in the engine cylinder. LabView is used to record the signal from the pressure transducer. Cylinder pressure data is collected for every 100 revolutions of the crankshaft. The fuel injection system is a common rail, and the injector has six injector holes (0.154 mm diameter per hole, and a spray angle of 154°). An electronic control unit that uses Gredi software is attached to the injection system. Brake fuel consumption is measured employing the AVL fuel economy gauge. This scale is based on the principle of gravity.

#### 2.3. Regulated and Unregulated Emissions Measurement

A Horiba-Mexa 7170DEGR gas analyzer was used for engine regulated exhaust gas analysis under various engine operating conditions. Non-dispersive infrared technology (NDIR) was used to measure CO and CO\textsubscript{2} concentrations. NO\textsubscript{X} emissions levels were measured using the chemiluminescence technique. The flame ionization detection technique

| Table 2. Fuel Used in the Recent Study Features |
|-----------------------------------------------|
| chemical formula | diesel (ULSD) | biodiesel (RME) |
| C\textsubscript{12}H\textsubscript{25,15}O\textsubscript{2} | C\textsubscript{15,38}H\textsubscript{26,15}O\textsubscript{2} |
| cetane number | 53.9 | 54.7 |
| density at 15 °C (kg/m\textsuperscript{3}) | 827.1 | 881.5 |
| viscosity at 40 °C (cSt) | 2.47 | 4.48 |
| flash point (°C) | 49 | 53 |
| boiling point (°C) | 278 | 242 |
| self-ignition temperature (°C) | 214 | 218 |
| lower calorific value (MJ/kg) | 43.4 | 37.5 |
| sulfur content (mg/kg) | ≥46 | ≥5 |
| aromatics (wt %) | 24.3 | \n| C (wt %) | 86.44 | 77.10 |
| H (wt %) | 13.56 | 12.05 |
| O (wt %) | 0 | 10.85 |
was employed to measure HC concentrations. An AVL-415 smoke meter was used in measuring the smoke emitted. A multigas 2030 FTIR spectrometer (Fourier transform infrared spectrometry) was employed to measure the unregulated emissions. Both units were equipped and installed by MKS Instruments UK, Ltd. Soot particles size distribution in the exhaust gases was measured using an electrostatic motion spectroscope (EMS). Both units were calibrated before starting the test every day.

2.4. Combustion Analysis. In this study, a heat release model used LabView software to download the pressure data in the combustion chamber to MATLAB and process it. The treatment is done by extracting the peak pressure, peak pressure angle, combustion onset, and apparent heat release rate (AHRR), without a specific heat transfer model.\textsuperscript{74} The total heat release rate is the loss due to a large part of this heat being excreted with the exhaust in addition to the other part moving through the cylinder walls. Equation 1 shows the AHRR, which is derived from the first law of thermodynamics and the energy balance equations in the combustion chamber.

\begin{equation}
\delta Q_{ch} = dU_f + \delta Q_{ht} + \delta W + \sum h_i dm_i
\end{equation}

Equation 1 has been simplified to

\begin{equation}
\frac{dQ_{ch}}{d\theta} = \frac{\gamma}{\gamma - 1} p \frac{dV}{d\theta} + \frac{1}{\gamma - 1} \frac{dp}{d\theta} + V \frac{dp}{d\theta} + \frac{dQ_{ht}}{d\theta}
\end{equation}

Also, this formula can be reformulated without correcting the heat loss from inside the combustion chamber through the cylinder walls:

\begin{equation}
\frac{dQ_{ch}}{d\theta} = \frac{\gamma}{\gamma - 1} p \frac{dV}{d\theta} + \frac{1}{\gamma - 1} V \frac{dp}{d\theta}
\end{equation}
Equations 1 and 2 were used to calculate the AHRR, and these two equations show a reasonable change in the energy applied to the piston. Previous studies explained in detail how temperature at certain limits clearly affects the formation of the peak heat release rate inside the combustion chamber.\textsuperscript{75,76} Peirce et al.\textsuperscript{77} indicated that the constant temperature is usually between 1.3 and 1.35. In the current study, two different types of fuel will be used under various engine operating conditions; therefore, the constant temperature \( T_{\text{c}} = 1.35 \) was adopted according to what was directed by ref \textsuperscript{77}. The AHRR can be considered as the sum of the net heat release rates at each crank angle (CAD), which was calculated from the start of the injection and is represented by the following relationship:

\[
\text{AHRR} = \sum_{\text{SOI}} \frac{\partial Q_{\text{in}}(i)}{\partial \theta (i)} \cdot k(i)
\]

Figure 2 shows a schematic description of the AHRR parameters. The data were controlled so that one medium pressure generation could be described by specifying a data set of 100 pressure cycles. This procedure reduces noise in results and preserves combustion properties. With exception of the combustion end region, the AHRR curve calculations were neither filtered nor averaged. As for the end-of-combustion zone, the arithmetic mean was used to enhance the consistency.

\[
\text{bsfc} = \frac{m_{\text{in}}}{P}
\]

### 2.5. Uncertainty Analysis.

The accuracy of the results depends on the extent to which the measured values agree with the true values, and the measurement error is expressed by the amount of inaccuracy. Accuracy represents the degree of reliability of measurements and results. It expresses the uncertainty in the measurement differences due to several factors that affect the accuracy of the measurement. The great difference between the concepts of accuracy in measurement and uncertainty must be underscored. In empirical studies, uncertainty analyses are used to quantitatively demonstrate accuracy. The uncertainty value is expressed by the addition and subtraction signs, and the signs indicate that the measured value is higher or lower than the expected value by the amount following the two signs. In empirical studies, uncertainty is analyzed to ensure that the measurements are within the acceptable range assuming that the accuracy is close to an ideal value. Uncertainty is directly related to measurement errors, whether they are random or systematic. The method of Klein and McClintock\textsuperscript{78} for uncertainty estimation was adopted in the current study. In this method, tests are used to determine the various experimental measurement errors using the following equation:

\[
W_R = \left( \frac{\partial R}{\partial x_1} \right)^2 + \left( \frac{\partial R}{\partial x_2} \right)^2 + \cdots + \left( \frac{\partial R}{\partial x_n} \right)^2 \right)^{0.5}
\]

\( W_R \) is the results’ uncertainty, \( R \) represents an independent variable function \( (x_1, x_2, ..., x_n) \), and \( (w_1, w_2, ..., w_n) \) expresses the independent variables’ uncertainties. In this study, the uncertainty in measurements of the engine’s performance and combustion characteristics (listed in Table 4) was

\[
W_R = \left[ (0.012)^2 + (0.18)^2 + (0.1)^2 + (0.9)^2 + (0.19)^2 
+ (0.22)^2 \right]^{0.5} = 1.776
\]

The emitted pollutant measurement uncertainty (listed in Table 5) was

\[
W_R = \left[ (0.15)^2 + (0.5)^2 + (0.5)^2 + (0.045)^2 
+ (0.34)^2 + (0.3)^2 + (0.11)^2 + (0.44)^2 
+ (0.12)^2 + (0.27)^2 + (0.14)^2 + (0.28)^2 \right]^{0.5} = 1.0588
\]

The test total uncertainty is

\[
W_R = \left[ (1.776)^2 + (1.0588)^2 \right]^{0.5} = 2.067
\]

This result (uncertainty < 3%) indicates high measuring accuracy.

#### 2.6. Test Procedure.

The combustion characteristics of the two fuels used during this study were evaluated using the single injection method, and during all experiments, the concentrations of regulated and unregulated emitted pollutants were measured. The pressure transducer prepares pressure measurements inside the cylinder and sends this data to the LabView program that analyzes it. Program results initialize AHRR, burning time, ignition delay, start of combustion, and bsfc.

### Table 4. Uncertainties of Engine Performance and Combustion Characteristics of the Measuring Instruments

| instrument            | measured parameter           | measurement limit | accuracy (%) | experimental uncertainty (%) |
|-----------------------|------------------------------|-------------------|--------------|-------------------------------|
| dynamometer           | engine torque                | 0–100 Nm          | -1.43        | ±1.12                         |
| pressure transducer   | combustion chamber pressure  | 0–250 bar         | -3.40        | ±0.18                         |
| AVL fuel gauge        | fuel consumption             | 125 kg/h          | +1.2         | ±0.1                          |
| entering air gauge    | air consumption              | 6.89 bar          | +0.77        | ±0.9                          |
| thermocouples         | temperature (inlet air, outlet exhaust gas, and ambient) | -200 to 2500 °C | -2.3         | ±0.19                         |
| flow meter            | fuel flow rate (kg/s)        | 1.44 kg/s         | -0.83        | ±0.52                         |
There are many conditions in which the engine can be tested. To eliminate these conditions, the engine has a rotation speed of 1500 rpm and it was loaded with four loads, which are 1.25, 2.5, 3.75, and 5 bar. These conditions may not fully represent the engine’s combustion features, but rather the operating conditions of an engine on city roads. The engine design optimum injection angle (9° bTDC) was used in the first set of trials to be the reference in comparison for both fuels. Practical experiments have been completed in the Center for Advanced Powertrain and Fuel Research (CAPF), College of Engineering and Design, Brunel University (United Kingdom). The test conditions inside the laboratory were set at an air temperature of 25 °C, air pressure of 1 bar at sea level, and relative humidity of 35%.

### 3. RESULTS AND DISCUSSION

#### 3.1. Combustion Characteristics

Figure 3A manifests the change in combustion chamber pressure and the released temperature with the crank angle change under high load [5 bar brake mean effective pressure (BMEP)] engine operating conditions and engine’s optimum injection timing (OIT) of 9° bTDC for ULSD and RME. The RME combustion chamber pressure curve increased ahead of the same curve for the ULSD utilization case. These results are confirmed by the

| Pollutant                  | Measurements Limit (ppm) | Instrument                        | Accuracy (%) | Uncertainty (%) |
|---------------------------|--------------------------|-----------------------------------|--------------|-----------------|
| CO                        | 0−745                    | Horiba-Mexa 7170DEGR gas analyzer | +0.78        | ± 0.15          |
| HC                        | 0−280                    | Horiba-Mexa 7170DEGR gas analyzer | −0.56        | ± 0.50          |
| NOx                       | 7−4100                   | Horiba-Mexa 7170DEGR gas analyzer | −1.14        | ± 0.50          |
| Smoke                     | 0−1                      | AVL-415 smoke meter               | −0.34        | ± 0.045         |
| \(C_2H_4O\) (acetaldehyde) | 0−135                    | multigas 2030 FTIR spectrometer   | +1.2         | ± 0.30          |
| \(C_2H_4O\) (acetone)      | 0−935                    | multigas 2030 FTIR spectrometer   | −0.044       | ± 0.11          |
| \(C_2H_2\) (acetylene)     | 0−465                    | multigas 2030 FTIR spectrometer   | −0.56        | ± 0.44          |
| \(C_2H_4\) (ethylene)     | 0−300                    | multigas 2030 FTIR spectrometer   | −0.087       | ± 0.12          |
| \(CH_2O\) (formaldehyde)  | 0−70                     | multigas 2030 FTIR spectrometer   | −0.60        | ± 0.27          |
| \(CH_4\) (methylene)      | 0−465                    | multigas 2030 FTIR spectrometer   | +0.45        | ± 0.14          |
| \(C_3H_6\) (propylene)    | 0−125                    | multigas 2030 FTIR spectrometer   | +0.62        | ± 0.28          |

**Table 5. Measured Emissions and Their Uncertainty**
similarly oriented AHRR curves. Figure 3B shows that the RME ignition delay period (IDP) is always shorter than that of ULSD fuel. These results can be traced back to the physicochemical properties of the RME fuel such as high cetane number and low vapor pressure. The IDP is highly dependent on the cetane number of the fuel. Additionally, increasing the combustion temperature in the cylinder enhances the self-ignition of the fuel, which reduces this period at medium and high loads. The results indicate that the ignition delay period decreased with the increase in the load of the two fuels due to the increase in cylinder pressure and temperature.

Figure 4 shows the measured combustion chamber peak pressure, which was relatively higher when ULSD is used compared to RME, for all engine loads tested. The amount of injected fuel inside the cylinder increased when the engine is overloaded, in order to raise the energy required to an acceptable level that runs the engine at a certain speed with such a load. The increased energy released from the fuel causes an increase in the combustion chamber pressure. For the two tested fuels, the highest peak HRR was at high loads (Figure 4). HRR was higher for diesel than for RME for all the studied loads. The HRR increment rates were 2.3%, 1.66%, 2.4%, and 4% in favor of ULSD at 1.25, 2.5, 3.75, and 5 bar, respectively. The peak temperature of diesel can be traced back to its higher calorific value compared to that of RME.

Another explanation for this result can also be given as Figure 5 illustrates that ULSD has a longer IDP, which increases the quantity of fuel burned in the pre-mixing stage. Although the pre-mixed combustion phase is short, the energy released during this period is higher than its counterparts in the diffusion phase. The combustion during the pre-mixed fuel stage is close to complete combustion due to the quality of the fuel—air mixing. For RME, oxygen concentration plays a vital role in reducing pyrolysis and increasing the oxidation, causing the ignition delay period to become shorter than that of diesel. The AHRR increases with increasing injection pressure, increasing the heat of combustion released, and increasing the pre-mixing phase. A higher AHRR means reduced CO and HC emissions and an increase in NOX concentrations. The results from Figure 5 show that with increasing engine loads, the pre-mixed combustion part decreases and the diffuse combustion part increases.

Figure 6 shows the bsfc variation at studied engine loads. The bsfc of both tested fuels increased at low load engine operation, as shown in Figure 6. The bsfc increased as the engine load was decreased due to the incomplete combustion of the fuel resulting from the combustion chamber’s low temperature. According to Figure 6, the results show that biodiesel bsfc had higher values than that of diesel, for all the tested loads. The fuel consumption increased by 9.4%, 12.5%, and 14.7% when the engine was running under engine loads of 1.25, 2.5, and 3.5 bar, respectively. It is reported that the bsfc increases when the engine was fed with biofuel including RME, and this can be brought back to its LHV in comparison with diesel (Table 1). These results are in agreement with a previous study by Fayad et al. In the case of high load (5
bar), due to the higher temperature of the combustion chamber, the viscosity of RME was decreased, which led to lower consumption compared to diesel.37

3.2. Regulated Emissions. Carbon monoxide is formed during the combustion process as an intermediate oxidation stage of carbon and appears in the exhaust as a result of incomplete combustion. This pollutant is released in the local fuel-rich areas inside the combustion chamber. These areas are formed in terms of their density and distribution, depending on the pressure and angle of injection. CO is also formed as a result of the low temperature inside the combustion chamber, which inhibits oxidation reactions. The experimental results showed that CO concentrations decreased when the engine was fueled with RME at all load values studied, as shown in Figure 7. An increase in the load causes the high combustion temperatures inside the combustion chamber as well as the high fuel injected quantity. The CO concentrations reduced by 46.8, 25.9%, 47.36%, and 30.9% at 1.25, 2.5, 3.75, and 5 bar engine load, respectively. This outcome agrees with a previous study.35

The best control of CO levels is through the fuel equivalence ratio inside the cylinder. The oxidation process slows down under low temperature conditions inside the combustion chamber when the engine is running at low loads. Also, operating the engine at rich equivalence ratios with a decrease in the oxygen required for oxidation will cause high CO levels even under high engine load operating conditions. The oxygen molecule in the RME composition promotes the combustion of local rich mixtures reducing the CO concentrations emitted. HC is formed inside the cylinders because of flame extinguishing on the cold cylinders’ walls as well as the low combustion gas temperature inside the combustion chamber.69

When the engine was fueled with RME and when the engine is overloaded, HC concentrations were noticed to be increased, as shown in Figure 8. The higher engine load causes the combustion chamber temperature to rise, which results in better oxidation reactions. The emergence of HC concentrations in the exhaust of the RME engine, which contains a high percentage of oxygen, can be traced back to the high viscosity of RME. This high viscosity causes spray penetration and delays fuel evaporation for a longer period and, in most cases when the combustion chamber temperature drops, wets the cylinder walls. This hydration produces high levels of HC.9,27 The results showed that RME emitted a higher HC level approximately by 3.07% in comparison with ULSD at lower loads (1.25 bar), and these levels escalated to a peak (at engine load of 3.5 bar) with an increase rate of about 38.3%. Also, at high engine loads (5 bar), RME emitted higher HC concentrations of about 15% than ULSD. This result is consistent with the results of many studies, some of which are

![Figure 7. CO level variation at different loads (BMEP).](http://pubs.acs.org/journal/acsodf)

![Figure 8. THC levels variation at studied loads.](http://pubs.acs.org/journal/acsodf)
mentioned in Table 1.\textsuperscript{36,38,41,45,56,63} Teoh et al.\textsuperscript{56} showed that variation in HC emissions is not related to engine speed or load but to the combustion chamber and fuel injection system designs. Valente et al.\textsuperscript{83} reported an increase in hydrocarbon concentrations with increased engine load as a direct result of combustion efficiency. The fuel/air mixture is enriched at high loads, which improves the combustion speed but provides an opportunity to extinguish the flame due to excessive cooling of the combustion chamber gases because of biodiesel vaporization. This result is consistent with previous studies,\textsuperscript{84,85} which were carried out on stationary diesel engines as in the current study. However, most of the published studies were conducted on car engines using an electronic engine control unit that makes self-adjustments to reduce the concentrations of pollutants emitted according to the combustion conditions and the characteristics of the fuel used. In this study, the conditions for processing diesel fuel in the engine were adopted and the injection conditions were not changed when using biodiesel as fuel. Therefore, the differences in the design of the combustion chamber and the fuel injection system can be considered the reason for the difference in the results of these emissions from one study to another, up and down.

One of the most important pollutants emitted from engines is particulate matter (PM), which consists of groups of organic and inorganic compounds. The fuels’ sulfur content plays an important role in the formation of PM.\textsuperscript{86} Figure 9A shows the change in PM particle diameters as the engine load changes when fuelled with USLD, while Figure 9B shows this change when the engine is running on RME. Most of the particles emitted from the USLD engine have a particle diameter ranging between 5 and slightly larger than 100 nm. The diameter of these particles decreases when the engine load increases, to be confined to a range of diameter from 5 to 40 nm. This result confirms the decrease in the size of these particles, sub-micron, with an increase in load. When the engine runs at low loads, due to the large pre-mixed

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{Load variation impact on particulate number levels and size distribution for (A) ULSD and (B) RME and (C) comparison between both fuels.}
\end{figure}
combustion part, these conditions do not allow the small particles to coagulate and aggregate to form larger particles. In the event that the engine is operating at high loads, it consumes more fuel during the propagation period, which results in the formation of additional concentrations of PM, which helps in increasing the coagulation rate and forming a larger particle number with larger particle diameters.

All oxygenated fuels of various types, whether biological or industrial, emit fewer particles and have a smaller diameter compared to diesel. This is confirmed by Figure 9C that compares the emitted PM particle diameters for both studied fuels. Several factors cause a reduction in the average particle size, including an increase in the combustion temperature inside the cylinder, which reduces the formation rate of PM, as well as the suppression of particle collision that prevents the formation of larger particles. Larger particles are formed by particles clumping together as the combustion gases cool. A decrease in the particles’ number and the agglomeration rate cause smaller particles to form with a decrease in the average particle diameter.

The use of RME causes nanostructured particles with greater oxidative potential, which promotes increased combustion

![Figure 10. Engine load variation impact on emitted smoke number.](image1)

![Figure 11. Engine load variation impact on NO\textsubscript{X}, NO, and NO\textsubscript{2} levels.](image2)
compared to PM formed from ULSD combustion. At higher loads, where more fuel is injected, the air/fuel ratio and excess oxygen decrease with it in addition to the combustion chamber high pressure and temperature, and all of these factors contribute to the intolerance of PM as well as intended nucleation growth. The higher oxygen content in RME improves combustion of locally rich equivalent ratios during the diffusion combustion fraction, resulting in reduced formation of particles with large diameters. The smoke number (SN) increased when the engine load was increased, and it was higher for the ULSD case as shown in Figure 10. The SN reduction rates from RME compared to that from diesel were 50%, 20%, 16.66%, and 33.9% for 1.25, 2.5, 3.75, and 5 bar, respectively. Smoke levels depend on several factors, including the equivalent ratio, the combustion temperatures inside the combustion chamber, and the good mixing of air and fuel. Local hypoxia in some locations of the combustion chamber causes high smoke concentrations. RME emits less smoke compared to USLD, especially at higher engine loads. The difference in smoke number for the two tested fuels at low loads is limited. The large presence of oxygen in RME is the primary reason for reducing the smoke number. This oxygen helps oxidize the fuel and reduce the smoke formation in the diffusion combustion stage. Therefore, the smoke number for RME is clearly reduced when the engine is running at high loads since in this case, more fuel is burned during the diffusion mode.

Another factor that can cause reduction in the smoke number is the low percentage of aromatics in RME as the formation of a large amount of smoke occurs in the diffusion burning mode. The pre-mixing state depends on the availability of hydrocarbons such as aromatics, alkenes, and alkanes. In this situation too, the effect of the length of the hydrocarbon chain is clear on smoke formation. Hence, the absence of aromatic substances from the chemical formula of RME had a positive effect on reducing the smoke number emitted from its engine.

NO\textsubscript{X} expresses a group of nitrogenous compounds like NO, NO\textsubscript{2}, NH\textsubscript{3}, etc., which result from the combustion process and emitted by the engine. For both RME and ULSD, the NO\textsubscript{X} emission levels increased, as shown by the curves of Figure 11, with increasing engine load. The figure shows the changes in NO\textsubscript{X}, NO, and NO\textsubscript{2} with the engine load. The NO\textsubscript{X} concentration formed inside the combustion chamber depends mainly on the temperature and air/oxygen. Hence, increased load causes an increase in NO\textsubscript{X} levels. For both fuels, NO\textsubscript{X} levels are roughly equal at low load such as 1.25 bar.

This result is similar to what was achieved by Chen et al. who observed relatively lower NO\textsubscript{X} concentrations for biodiesel compared to diesel at lower loads for low and medium engine speeds (low or medium combustion chamber temperatures). The authors indicated that the reason for this decrease could be attributed to the high viscosity and negative effects of the distillation temperature on spray quality and the homogeneity of the air−fuel mixture at low loads and low and
medium speeds. With increased engine load, NOx emissions from the RME engine outperformed those from a diesel engine. The increase in NOx emissions was 12% at an engine pressure of 2.5 bar in favor of diesel. Here, it is expected that the cooling effect of biodiesel evaporation reduced the temperature of the gases formed inside the combustion chamber, which hinders the NOx formation. The NOx levels for both fuels converged at 3.75 bar with a slight rise in RME. The highest emission difference achieved was 13% in favor of RME when carrying a 5 bar engine load (Figure 11). The main reason to justify this rise is the increase in the combustion chamber temperature and the increase of the amount of fresh air inside the combustion chamber as the engine load increased. Therefore, the high temperature of the combustion chamber promoted the formation of higher concentrations of NOx. When working with RME, the oxygen abundance and the high combustion temperature produced higher levels of NOx. When working with ULSD, the ignition delay period for this fuel is longer and the pre-mixed combustion fraction is larger, which increases the combustion temperature, causing high NOx levels for the low-load condition. Pearce et al. confirmed that RME combustion emits lower NOx levels compared to ULSD under the low-load conditions at the pre-mixed combustion fraction condition. However, the exact opposite happens at high loads. The researchers correlated these results for both fuels with variation in combustion duration, delay period, and pre-mixed combustion fraction. Also, in this study, the use of fixed ignition timings that suited with diesel combustion may be advanced for RME. As a result, higher levels of NOx were emitted in the exhaust.

3.3. Nanoparticle Size. Among the various suspended particles in the air, nanoparticles with diameters ranging from 1 to 100 nm are the most dangerous. The time for these particles to remain suspended in the atmosphere is up to 1 week. While the coarse particles are removed from the atmosphere through their deposition, the smaller particles are not deposited for a period of time during which they are collected and agglomerated. The long stay of particles of minute size in the atmospheric air poses many risks to human health as it is considered a carcinogen. The time of human exposure to ultrafine particulate matter significantly increased, especially in indoor environments (homes and offices) in which most people spend their time. Most of these nanoparticles are emitted by human activities such as exhaust from internal combustion engines, power plant chimneys, and industrial fires.

Nanoparticles are formed due to incomplete combustion based on solid nucleation (sulfur particles help greatly in its formation), and their sizes differ due to heterogeneous and homogeneous nucleation during the formation process. The reasons for the homogeneity and heterogeneity are still unclear. Most of the nanoparticles are formed inside the cylinder in the fuel-rich region due to incomplete combustion resulting from its low temperature. Nanoparticles are formed due to incomplete combustion based on solid nucleation (sulfur particles help greatly in its formation), and their sizes differ due to heterogeneous and homogeneous nucleation during the formation process. The reasons for the homogeneity and heterogeneity are still unclear. Most of the nanoparticles are formed inside the cylinder in the fuel-rich region due to incomplete combustion resulting from its low temperature.

Figure 12 shows the cumulative concentration number (CCN) during the nucleation and accumulation mode of the studied loads. Particles with diameters smaller than 40 nm represent the nucleation mode, while particles larger than this measure represent the accretion mode. Figure 12a shows that the CCN for the nucleation mode decreases with increasing load, while the CCN for the accumulation mode increases with increasing load (Figure 12b). At high loads, the accumulation of particles increases with the increase in the coagulation rate, and this situation results in an increase in the rate of larger diameter particle formation. From RME combustion, fewer particles are formed during the accretion mode (diameters greater than 40 nm).

The reason can be traced back to the abundance of oxygen in the RME formula, which enhances the combustion quality in the fraction of the flame spread out in the local rich equivalence ratio regions within the cylinder. This enhancement increases the oxidation rate of the formed fine particles. Also, the absence of aromatics in the RME formulation reduced the activated PM molecules during the accumulation.
mode. The result obtained (reduction of PM formation during the accumulation mode when the engine is running on RME) is consistent with the findings of refs 79, 103−105. When using RME, there was a decrease in the total number of particles (Figure 12c) when calculating the number of particles for the accumulation and nucleation method. The use of RME not only caused a decrease in PM but also caused the CCN of the total particles formed to increase.

3.4. Unregulated Pollutants. Measurements of the unregulated pollutant levels (in Figure 13) show very low values as most of these pollutants have a concentration of less than 8 ppm. The emitted aldehydes are intermediate products found in hydrocarbon or oxygenated fuels.\(^\text{106}\) Formaldehyde (CH\(_2\)O) is the most commonly measured aldehyde in exhaust gases, and its concentration diminution with increasing engine load for both fuels was tested. Formaldehyde is also an intermediate combustion product, which results in the combustion chamber temperature’s significant increase. The results show that the measured formaldehyde levels were increased when the engine was run on RME by 1.47%, 1.09%, 48.8%, and 74.8% for 1.25, 2.5, 3.75, and 5 bar, respectively, compared to the diesel. This result was confirmed by previous works.\(^\text{107−110}\) The same references indicated that under low-load conditions, high levels of formaldehyde are also emitted (6.9 and 6.8 ppm at 1.25 and 2.5 bar). This means that formaldehyde is formed at low temperatures, and its formation is in areas where the air/fuel mixture is fat-free. Guerreiro et al.\(^\text{111}\) mentioned that the relatively high concentration of formaldehyde is due to the presence of an amount of short-chain (saturated) methyl esters in biofuels that form the shorter chain carbonyls during combustion.

The curves of Figure 13 show that ethane (C\(_2\)H\(_6\)) does not change significantly with the change in the load of the used diesel, but when working with biodiesel, concentrations that can be measured only appear at engine loads above 5 bar. The levels of ethylene (C\(_2\)H\(_4\)), which results from the pyrolysis of both ULSD and RME, decreased. Ethylene is the simplest unsaturated alkene that can be considered after acetylene. Ethylene concentrations decreased when the engine was running on diesel fuel at high loads while when the engine was running on biodiesel, the ethylene concentration increased with increased load and reached its maximum values when the engine was loaded at 3.75 bar.

The behavior of the emitted propylene (C\(_3\)H\(_6\)) is similar to that of HC. It increases with an increase in engine load when working with RME and decreases when the engine is running on diesel. This behavior is due to the same reasons that explain the case of HC.\(^\text{112}\) When RME fueled the engine, the C\(_3\)H\(_6\) increment rates were 88.2%, 100%, 250%, and 506% for MBEP 1.25, 2.5, 3.75, and 5 bar, respectively, compared to ULSD. As for the unsaturated alkene (CH\(_x\)) and acetylene (C\(_2\)H\(_2\)), they have the same orientation. Ethylene, acetylene, and propylene are considered hazardous materials due to their high reactivity and toxicity. These substances are produced from pyrolysis, and then they react to form polycyclic aromatic hydrocarbons (PAHs), which are the nuclei of PAM molecules.\(^\text{109−112}\) The levels of C\(_3\)H\(_6\), C\(_2\)H\(_6\), and C\(_2\)H\(_2\) are affected by the equivalence ratio and temperature of combustion. At high load conditions, the high combustion chamber temperature oxidizes the pyrolysis products. In the same conditions, the rich equivalence ratio causes the pyrolysis products to rise. The increment rates for ethylene when RME was used were 26%, 47%, 105.47%, and 137.28% for engine MBEP of 1.25, 2.5, 3.75, and 5 bar, respectively, compared to ULSD. When RME was used, methane concentrations at 1.25 and 2.5 bar were less than those when ULSD was used by 16% and 4.3% while at 3.75 and 5 bar operation, its concentrations exceeded those when ULSD was used by 271.4% and 400%, respectively. Acetylene concentrations for RME started lower than that emitted by ULSD at 1.25 and 2.5 bar by 33.3% and 26.6%, respectively. When the loads increased to 3.75 and 5 bar, RME emitted higher levels of acetylene than ULSD by 17.39% and 30.23%, respectively.

Isocyanic acid (HNCO) is a simple and stable chemical compound composed of hydrogen, carbon, oxygen, and nitrogen atoms, which are the most common elements in organic chemistry. This acid is produced by reactions between H\(_2\), NO, and CO. For ULSD, when the engine load is increased, the isocyanic acid concentrations were decreased (3.9, 3.5, 0.5, and 0.4 ppm for 1.25, 2.5, 3.75, and 5 bar, respectively). However, when biodiesel is used, the rise in isocyanic acid concentrations with load increasing was limited (4.1, 4.3, 5.5, and 3.0 ppm for 1.25, 2.5, 3.75, and 5 bar, respectively). An increase in the engine load leads to a significant increase in the temperature of the combustion chamber. This state increases the reaction rate of H, O, and N molecules, which reduces the formation of this acid.\(^\text{62}\) In the case of using RME biofuel, there is more oxygen inside the combustion chamber, which helps to increase the relative formation of isocyanic acid.

4. CONCLUSIONS

RME is an environmentally friendly and green fuel that can operate compression ignition engines with very minor modifications to the engine design. In the current study, the combustion properties, the concentrations of regulated and unregulated pollutants, and the size of the nanoparticles emitted from the engine operation were tested using RME. The obtained results are compared to ULSD under the same engine operating conditions. The experimental results demonstrated that the AHRR of RME fuel is higher than that of ULSD, and the IDP was always shorter than the ULSD ones by 2 to 3 CAD. In addition, it was found that the diesel has a higher heat release rate than RME. The bsfc from RME combustion was higher than that from diesel by 9.4% at low loads and increased to 11.3% at high loads.

The exhaust gas emission results showed that CO emitted levels when the engine is running on RME were significantly lower than on ULSD by 46.3%, and this decrement retracted to 30.9% at high loads. HC concentrations increased when the engine was running on RME to reach a value about 38.3% higher than on ULSD at high loads. Most of the output PM from a diesel engine has a particle size from 5 to 100 nm, while for the RME engine working condition, the particle size was from 5 to 40 nm. It was observed that the nanoparticle sizes decreased with the increase of engine load for both fuels. The smoke number for ULSD was higher than for RME, and this number increased with increasing load. The results also revealed that NO\(_X\) concentration was relatively high (13%) in the case of RME and in both fuels increased with increasing engine load. Measurements of formaldehyde, ethane, methane, acetylene, ethylene, propylene, and isocyanic acid emissions showed the presence of these harmful substances at very low concentrations (less than 8 ppm). At 5 bar MBEP, the formaldehyde, methanol, acetylene, ethylene, propylene, and isocyanic acid concentrations were higher than for ULSD by
The authors declare no competing financial interest.

Notes

The authors declare no competing financial interest.

NOMENCLATURE

bsfc brake specific fuel combustion
EOC end of combustion
EOPMB end of pre-mixed burn
Hiidmi losses by the crevices
ID ignition delay
k resolution of the heat release rate expressed in 1/measured point in 0.125 CAD
m o fuel mass flow rate
P engine output power
p in-cylinder pressure
PMBF pre-mixed burn fraction
OIT optimum injection timing
Q is convective heat transfer to the cylinder walls
SOC start of combustion
SOI start of injection

Us internal energy
V cylinder volume
W work output
γ adiabatic index (specific heats ratio)
θ crank angle degree

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