Insight into Nanoparticle-Number-Derived Characteristics of Precharged Biodiesel Exhaust Gas in Nonthermal Plasma State

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ABSTRACT: The utilization of biodiesel as an alternative partial replacement of diesel fuel was shown to improve exhaust emissions from diesel engines. Waste cooking oil biodiesel (WCO) has also gained more attention due to edible biofuel supply and the environment. In this study, a nonthermal plasma (NTP) technique was applied to be equipped into the after-treatment system of a four-cylinder diesel engine at medium- and high-load conditions. The exhaust gases in the NTP state from the combustion of WCO and diesel (D100) fuels were partially drawn by spectrometers and nanoparticle-number-derived characteristics were analyzed. The particle number, area, and mass concentrations were in log-normal distribution over equivalent diameters, and they were higher at high load. The concentration of the particulate matter (PM) was lower but was larger in size when the NTP charger was activated due to coagulation principally owing to WCO’s number and surface area. The total particle masses were lower for WCO at the two load conditions tested. During NTP charger activation, the mass mean diameters were increased by maximum values of 24.0% for D100 and 5.5% for WCO. The PM removal efficiencies were maximized by 10.8% for D100 and 16.7% for WCO when the NTP charger was in use, and the WCO exhaust was dominantly seen to simultaneously reduce NOx and PM emissions.

INTRODUCTION

The usage of biodiesel as a renewable fuel substitution for diesel engine has extensively increased in conjunction with continuous improvement in production techniques, as well as physical and chemical properties. One of the main advantages of biodiesel is the reduction of exhaust gas emission in terms of soot precursor and particulate matter derivatives released. A biodiesel contains very low sulfur content and can be degraded depending on the surrounding interaction. Biodiesel has been fueled to almost all types of compression ignition (CI) engines and found to improve the performance and tribological aspects.

Depending on production methods, biodiesel or fatty acid (m)ethyl ester is renewable and mainly derived from various feedstocks. Different biofuel generations are dependent on their source. The first biofuel generation is mainly from animal fats and vegetable oils. Nowadays, a more rigid regulation in food waste management is being enforced. WCO is becoming a prospective raw material for producing biodiesel and can drastically reduce some emissions from diesel engines in certain operating conditions. Therefore, waste cooking oil (WCO) can reduce the amount of food waste in several countries.

The application of WCO biodiesel in CI engines has been widely explored in many aspects. In a light-duty diesel engine fueled by WCO biodiesel–diesel blends, Plamondon and Seers parametrically studied certain pilot and main fuel injection strategies that affected engine performance. Tayari et al. assessed the engine performance of three different biodiesel generations. These diesel engines were found to worsen by biodiesel fueling prior to recalibration for fuel injection strategies. A varying compression ratio of a CI engine can elevate superior complete combustion of the WCO biodiesel due to oxygenated composition. Owing to these reasons, various types of feedstock for biodiesel production have been extensively studied for particulate matter (PM) after combustion in CI engines.

PM formation in low-load combustion is critical for CI engines apart from that at full load. Jung et al. evaluated the exhaust PM for biodiesel in low-temperature combustion that can occur by applying low load to an engine. PM and other unregulated gaseous emissions were influenced by an oxygenated fuel such as WCO biodiesel. At a microscopic level,
Wei et al.\textsuperscript{17} depicted the nanostructure and investigated the volatility of particles emitted from a direct-injection (DI) diesel engine fueled by the WCO biodiesel. The consequent findings resemble the particle volatility of a DI diesel engine previously recorded in the report by Lu et al.\textsuperscript{18} Particle number-size distribution and other unregulated emissions were found to improve under specific running conditions in a diesel bus fueled with biodiesel blends.\textsuperscript{19} However, the engines fueled by the WCO biodiesel still suffer from PM and nitrogen oxide (NO\textsubscript{x}) emissions.\textsuperscript{20} The well-known PM–NO\textsubscript{x} trade-off emissions have been sought for simultaneous mitigation by numerous techniques.\textsuperscript{21}

Nonthermal plasma (NTP) technology is one of the viable techniques that can mitigate combustion-generated emissions.\textsuperscript{22} Owing to the creation of a plasma field that is not in thermodynamic equilibrium, an NTP device is often used in applications that involve particles of dust or soot.\textsuperscript{23} A dielectric barrier discharge (DBD) is created under the NTP state of substance between electrodes and separated by an electrical insulator.\textsuperscript{24}

An NTP charger was applied to after-treatment systems for reducing pollution particularly for PM.\textsuperscript{25} On top of that, NO\textsubscript{x} emissions were improved by electron-produced thermocoils and ozone-generated catalytic oxidation.\textsuperscript{26} Hydrocarbon fuel combustion products can be lowered for volatile organic compounds (VOCs) under the NTP state.\textsuperscript{27} A 480 W dual flat rectangle electrode NTP charger was used to remove PM from the burning diesel fuel at 58\% maximum reduction.\textsuperscript{28} At low temperatures, an NTP device was also incorporated with a diesel particulate filter (DPF) to efficiently oxidize PM.\textsuperscript{29} In the diesel NO\textsubscript{x} after-treatment reported by Yoshida,\textsuperscript{30} the combined techniques of temperature swing adsorption, NTP, and exhaust gas recirculation were employed to expedite NO\textsubscript{x} exclusion by converting nitric oxide to nitrogen dioxide. Based on thermogravimetric analysis, the findings reported in Wang et al.\textsuperscript{31} disclosed a 24.36\% decrease in the soluble organic fraction (SOF) of PM after NTP treatment. The scanning electron microscope (SEM) observations depicted the declination degree of PM agglomeration and a smaller PM equivalent diameter.

In the literature reviewed, the NTP treatment for diesel exhaust gas has been utilized in different applications. Providing an NTP charger to the exhaust of the engine may cause a reduction of combustion-related emissions, i.e., NO\textsubscript{x} and PM. Most studies have used NTP technology as an after-treatment device for diesel-fueled engines. However, limited work has been commissioned for the NTP application in WCO-biodiesel-fueled engines.\textsuperscript{32,33} Biodiesel can give a lowered PM emission but high NO\textsubscript{x} emission. In addition, less information is available on nanoparticle number distribution with derived physical parameters and NO\textsubscript{x}–PM trade-off emissions from this application. Other consequences have not yet been revealed according to these issues.

The first objective of this work is to investigate a nanoparticle number-size distribution and the total number of the PM in the WCO biodiesel exhaust gas in the NTP state. Meanwhile, the second objective is to identify the calculated surface area-size distribution and total surface area of the PM as this can confirm the behavior of the PM after NTP charging. The third objective is to learn the response of the NO\textsubscript{x}–PM trade-off emissions in the exhaust gas charged to the NTP state. To deal with these objectives, the scope of this experimental study is set to commission on a multicylinder diesel engine at a low engine speed of 1500 rpm at medium- and high-load conditions without engine recalibration. The PM number is characterized through the samples measured by a scanning mobility particle sizer and an optical particle sizer under controlled conditions. The obtained results will be compared and discussed in detail for both diesel (D100) and waste cooking oil biodiesel (WCO) fuels as well as with and without-NTP chargers. Subsequently, the rudimentary information will be given as a recommendation for future reference.

RESULTS AND DISCUSSION

Total Particle Number and Concentration–Size Distribution. Figure 1 shows the particle number concen-

![Graph (a)](https://doi.org/10.1021/acsomega.1c06597)

![Graph (b)](https://doi.org/10.1021/acsomega.1c06597)

Figure 1. Particle number–size distribution at (a) medium-load and (b) high-load conditions.
to decline to a greater extent compared to that of D100 when the NTP charger was activated. The particle sizes in terms of equivalent diameter cannot be clearly seen for these graphs, and they will be summarized and discussed later in terms of the total particle number concentration.

Figure 2 shows the plots of the total particle number concentration corresponding to the count mean diameters (CMDs). The total particle number concentration \(N\) was determined from all size ranges given by the equation

\[
N = \sum n_i
\]

where \(n_i\) is number concentration and \(u\) and \(l\) are minimum and maximum particle sizes, respectively. Meanwhile, the CMD was calculated as \(\text{CMD} = \frac{\sum n_i D_i}{N}\), where \(D_i\) is the equivalent diameter.

For both fuels, the total particle number concentrations were higher at a higher engine load (Figure 2). When the NTP charger was activated, the total particle number concentrations were shown to reduce for both fuels and loads. At a medium load, the reductions in the total particle number concentration were \(9.7 \times 10^6\) and \(3.0 \times 10^7\) \(m^{-3}\) for WCO and D100 fuels, respectively. Also, at a high load, the reductions in the total particle number concentration were \(4.9 \times 10^7\) and \(3.5 \times 10^7\) \(m^{-3}\) for WCO and D100 fuels, respectively. In general, these accounted for the reductions of 71.5\% and 56.0\% in CMD for D100 and WCO, respectively, when the NTP charger was used. The results showed that the total number concentrations of WCO declined to a greater extent compared to those of D100 at a high load when the NTP charger was activated. Meanwhile, the opposite trend was observed at a low engine load.

In Figure 2, the particles are bigger in size as the CMD values are shown to increase for both fuels and loads when the NTP charger is activated. Without the use of the NTP charger, the CMDs for WCO and D100 fuels were in the range of 49.7–56.7 and 52.4–56.8 nm, respectively, at medium to high loads. When the NTP charger was in use, at a medium load, the CMDs increased in size to 88.4 and 65.0 nm for WCO and D100 fuels, respectively. Also, at a high load, the CMDs increased to 59.9 and 71.5 nm for WCO and D100 fuels, respectively. Overall, these accounted for the increments of 24.2–26.0 and 20.6–56.0\% in CMD for D100 and WCO, respectively, when the NTP charger was in use. When the NTP charger was activated, the CMD of WCO was larger compared to that of D100, particularly at a high load while the opposite trend was observed at a low engine load.

The attained behavior that the particle number concentration is reduced with increasing particle diameter is associated with coagulation while using the NTP charger. Fuel type and engine load are among various parameters concerned. The particles comprising elemental carbon (EC) and VOC seem to be affected in the NTP state, especially for WCO, whereas its EC portion is lesser.\(^{34}\) PM in the NTP state can reduce the EC with WCO and D100 fueling, particularly at a medium load where the exhaust temperature was not that high. The obtained results are in-line with the findings reported in Chae.\(^{35}\) In addition, the particle concentration results show a great reduction performance for the small size particles, which indicates that the NTP charger can cause the low-temperature oxidation of PM.\(^{36}\) The amount of PM in terms of carbon is reduced by plasma chemistry reactions through the ionization of nitrogen dioxide (NO\(_2\)), a component of NO\(_x\).\(^{36}\) The possible mechanisms of PM and NO\(_x\) reduction are proposed as follows: \(^{31,36,37}\)

\[
\begin{align*}
\text{C} + 2\text{NO}_2 & \rightarrow \text{CO}_2 + 2\text{NO} \\
\text{C} + \text{NO}_2 & \rightarrow \text{CO} + \text{NO} \\
2\text{C} + \text{NO}_2 & \rightarrow 2\text{CO} + 0.5\text{N}_2 \\
2\text{C} + 2\text{NO}_2 & \rightarrow 2\text{CO}_2 + \text{N}_2
\end{align*}
\]

These reaction mechanisms can proceed at low temperatures (under 200 °C). In addition, NO\(_2\) can also be converted to nitrogen for PM reduction reactions. These are the synergistic effects of NTP on PM and NO\(_x\) at low temperatures.

At a larger size, the reduction performance of particle number declined; this situation occurred because the VOC cannot oxidize at low temperatures. From the particle concentration results, it is clear that the coagulation of the nucleation mode particles was in a transformation phase to the accumulation mode particles that occurred by the small particles passing through the electrostatic force to form larger particles.\(^{23}\) This phenomenon can reduce the performance of the NTP state in the range of the accumulation mode particle.\(^{38}\)

**Estimated Particle Surface Area.** Figure 3 shows the calculated particle surface area concentration distribution over the range of equivalent diameter in logarithmic scale from the exhaust of the engine fueled with D100 and WCO at 1500 rpm for medium and high loads. The particle area concentration \(A\) in each size range was estimated by the equation

\[
A = \sum a_i
\]

where \(a_i\) and \(D_i\) are number concentration and equivalent diameter, respectively. Regardless of the fuel type and engine load, the particle area concentrations were in log-normal distribution stretching over the equivalent diameters between 10 and 1000 nm, covering both nucleation and accumulation modes. For both fuels, the particle area concentration distributions were higher for the higher engine load. The activation of the NTP charger reduced the particle area concentration curves for both fuels and loads. The WCO particles were shown to have a lower area concentration than the D100 particles.

Figure 4 shows the plots of the total particle surface area concentration versus area mean diameters (AMDs). The total particle area concentration \(A\) was determined from all size ranges by the equation

\[
A = \sum a_i
\]

where \(a_i\) and \(D_i\) are surface

\[
A = \sum a_i
\]

where \(a_i\) and \(D_i\) are surface
area concentration and minimum and maximum particle sizes, respectively. Meanwhile, AMD was calculated as 
\[ \text{AMD} = \sum A_{MD} a_{D, \text{up}}, \]
where \( D_p \) is the equivalent diameter.

For both fuels, the total particle area concentrations were higher for the higher engine load (Figure 4). When the NTP charger was activated, the total particle area concentrations were shown to reduce but increase in size for both fuels and loads. The total particle areas were greater for D100 at both loads. At a medium load, the reductions in the total particle area concentration were \( 2.0 \times 10^{-6} \) and \( 1.3 \times 10^{-4} \) m\(^{-3}\) for WCO and D100 fuels, respectively. Also, at a high load, the reductions in the total particle area concentration were \( 1.9 \times 10^{-4} \) and \( 3.0 \times 10^{-4} \) m\(^{-3}\) for WCO and D100 fuels, respectively. In general, these accounted for 39.7–55.4 and 1.4–39.0% reductions in the total area concentration for D100 and WCO, respectively, when the NTP charger was in use.

As shown in Figure 4, the AMD values increase for both fuels and loads when the NTP charger is activated. Without the use of the NTP charger, the AMDs for WCO and D100 fuels were in the ranges of 78.6–88.7 and 76.9–86.0 nm, respectively, at medium to high loads. When the NTP charger was in use, at a medium load, the AMDs increased to 125.8 and 96.0 nm for WCO and D100 fuels, respectively. Also, at a high load, the AMDs increased to 85.9 and 101.2 nm for WCO and D100 fuels, respectively. Overall, these accounted for the increments of 17.6–24.9 and 9.3–41.8% in AMD for D100 and WCO, respectively, when the NTP charger was in use. When the NTP charger was activated, the AMD of WCO was larger compared to that of D100.

**Calculated Total Particle Mass and Concentration–Size Distribution.** Figure 5 shows the calculated particle mass concentration distribution over the range of equivalent diameters in logarithmic scale from the exhaust of the engine fueled with D100 and WCO at 1500 rpm for medium and high loads. The particle mass concentration \( m \) in each size range was estimated by 
\[ m = \rho \pi D_p^3 n / 6, \]
where \( n, D_p \), and \( \rho \) are the

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**Figure 3.** Particle surface area concentration–size distribution at (a) medium-load and (b) high-load conditions.

**Figure 4.** Total particle surface area concentration versus the area mean diameter.

**Figure 5.** Particle mass concentration–size distribution at (a) medium-load and (b) high-load conditions.
number density, respectively. For the purpose of comparison, the particle density of 1.0 kg/m³ was chosen and used for calculation. Generally, regardless of the fuel type and engine load, the particle mass concentrations were in log-normal distribution extending over the equivalent diameters between 10 and 1000 nm, covering both nucleation and accumulation modes. For both fuels, the particle mass concentration distributions were higher for the higher engine load. The activation of the NTP charger reduced the particle mass concentration curves for both fuels and loads. The WCO particles were shown to have lower mass concentration distribution than the D100 particles.

Figure 6 shows the plots of the total particle mass concentration versus mass mean diameters (MMDs). The total particle mass concentration \( M \) was summarized from all size ranges as \( M = \sum_{n} m_{l} m_{l} \), where \( m_{l} \), \( l \), and \( u \) are mass concentration and minimum and maximum particle sizes, respectively. Meanwhile, MMD was calculated as \( \text{MMD} = \frac{\sum_{n} m_{D_{l}} m_{D_{l}}}{M} \), where \( D_{l} \) is the equivalent diameter.

For both fuels, the total particle mass concentrations were higher for the higher engine load (Figure 6). When the NTP charger was activated, the total particle mass concentrations were shown to reduce but increase in size for both fuels and loads. The total particle masses were higher for D100 for both loads. At a medium load, the reductions in the total particle mass concentration were \( 1.5 \times 10^{-9} \) and \( 3.1 \times 10^{-9} \) kg m⁻³ for WCO and D100 fuels, respectively. Also, at a high load, the reductions in the total particle mass concentration were \( 1.8 \times 10^{-9} \) and \( 3.2 \times 10^{-9} \) kg m⁻³ for WCO and D100 fuels, respectively. In general, these accounted for the reductions of 45.8–84.9 and 33.0–83.2% in the total mass concentration for D100 and WCO, respectively, when the NTP charger was in use.

In Figure 6, the MMD values are shown to increase for both fuels and loads when the NTP charger was activated. Without the use of the NTP charger, the MMDs for WCO and D100 fuels were in the ranges of 91.2–100.4 and 87.3–97.8 nm, respectively, at medium to high loads. When the NTP charger was in use, at medium load, the MMDs increased to 102.2 and 108.3 nm for WCO and D100 fuels, respectively. Also, at high load, the MMDs increased to 96.2 and 113.8 nm for WCO and D100 fuels, respectively. Overall, these accounted for the increments of 16.4–24.0 and 1.8–5.5% in MMD for D100 and WCO, respectively, when the NTP charger was in use. When the NTP charger was activated, it was noted that the MMD of WCO was less dominant compared to that of D100.

\( \text{NO}_x-\text{PM} \) Trade-off Emission Response. Figure 7 shows the \( \text{NO}_x \) and PM pollutants in the exhaust emissions of the engine fueled by D100 and WCO at 1500 rpm for medium and high loads. In general, during NTP charger deactivation, the engine emitted higher \( \text{NO}_x \) but lower PM concentrations for WCO than those for D100. This trend can also be observed for both engine loads, with higher concentrations clearly seen at high loads. With the activation of NTP, both PM and \( \text{NO}_x \) emissions were drastically reduced for both loads. In this manner, it is possible to use the NTP charger to break this \( \text{NO}_x-\text{PM} \) trade-off. However, an optimization between fuel parameters and NTP is rudimentary to maintain this trade-off to be within the scope of acceptability.

In terms of pollutant emission quantity as seen in Figure 7, at medium loads, the reductions in \( \text{NO}_x \) concentration were 0.25 g/kW·h and 0.17 g/kW·h for WCO and D100 fuels, respectively. Also, at high loads, the reductions in \( \text{NO}_x \) concentration were 0.53 g/kW·h and 0.49 g/kW·h for WCO and D100 fuels, respectively. In general, these accounted for the \( \text{NO}_x \) reductions of 21.5–27.9% for D100 and 24.5–34.3% for WCO when the NTP charger was in use. Also, in Figure 7, when the NTP charger was in use, at medium loads, the PM pollutants were reduced by 0.062 g/kW·h and 0.042 g/kW·h for WCO and D100 fuels, respectively. At high loads, the PM pollutants also declined by 0.055 g/kW·h and 0.054 g/kW·h for WCO and D100 fuels, respectively. Overall, these removal efficiencies accounted for the PM reductions of 10.1–10.8% for D100 and 11.5–16.7% for WCO when the NTP charger was in use. In summary, when the NTP charger was activated, WCO was dominantly seen to reduce \( \text{NO}_x \) and PM exhaust emissions simultaneously compared to that of D100.

The PM reduction when activating the NTP charger is already well described as a result of particle number. Meanwhile, the \( \text{NO}_x \) reduction through the plasma chemistry reactions of the molecule dissociation is by electron collision in
the discharge plasma,\(^{37}\) as described by the following equations

\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \] (5)

and

\[ 2\text{NO}_2 \rightarrow \text{N}_2 + 2\text{O}_2 \] (6)

Furthermore, other reactions also occurred in a moist environment\(^{40,41}\) following these equations

\[ \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+ \] (7)

\[ \text{NO} + \text{OH}^- \rightarrow \text{HNO}_2 \] (8)

\[ \text{NO}_2 + \text{OH}^- \rightarrow \text{HNO}_3 \] (9)

and

\[ \text{NO} + \text{H}_2\text{O} \rightarrow \text{NO}_2 + \text{OH}^- \] (10)

From the experimental results, the NTP charger in this experimental study can reduce \(\text{NO}_x\) covering 21.5–34.3\% for D100 and WCO fuels in both loads, which is a lower removal efficiency compared to that in the previous research.\(^{42,43}\) The lower removal efficiency for this NTP system is because of two main reasons. The first reason is a gas residence time in the NTP device.\(^{44}\) The diesel engine exhaust gas passed through the NTP reactor at a slightly higher speed. To increase the removal efficiency, the residence time of the exhaust gas was suggested to be more than 3.3 s.\(^{45}\) The second reason is that the removal efficiency has a direct relationship with the NTP energy density.\(^{46}\) However, in this experiment, the NTP charger for WCO can break the well-known \(\text{NO}_x\)-PM trade-off emissions from the diesel engine exhaust.

Compared to other catalytic after-treatment systems, the main advantage of the NTP technique is that there is no internal pressure drop, for example, accumulated soot in DPF.\(^{47}\) The pressure drop in the after-treatment system can affect the geometry of particle release from the diesel engine by increasing the engine exhaust back-pressure level.\(^{48}\) In terms of energy consumption, the NTP charger can reduce the PM (mass) by the maximum of 16.7\% under the maximum power consumption of 60 Watts (data not shown in detail). The consumed power of the NTP charger is only 0.001\% of the engine output power, which is practically acceptable and viable in real usage.

For the PM emissions after the NTP treatment, the particle number concentration is clearly reduced by condensation and coagulation but the particle size is slightly increased. The latter can occur from the particle growth through coagulation when the exhaust passes through the NTP charger. The removal performance of the NTP charger is slightly different from theoretical NTP derived in Yamamoto et al.,\(^{35}\) which may be caused by voltage and frequency of the NTP reactor.

### CONCLUSIONS

This study presents the analysis of particle-number-derived characteristics of the NTP exhaust gases from a diesel engine running on WCO compared with that running on D100 at 1500 rpm at medium and high loads. The exhaust samples were collected before and after passing through the NTP reactor. Generally, the particle number, surface area, and mass concentrations were in log-normal distribution expanded over the equivalent diameters covering both nucleation and accumulation modes. Specifically, the conclusions can be drawn as follows.

All total particle number concentrations were higher for the high engine load. When the NTP charger was activated, the total particle number concentrations were shown to reduce by the maximum values of 91.9\% for D100 and 95.4\% for WCO. The particulates were bigger in size due to coagulation when the NTP charger was activated. When the NTP charger was activated, the CMD of WCO was larger compared to that of D100. All trends of the total particle area concentrations corresponded to those of the particle number concentrations.

The total particle mass concentrations were generally higher for the higher engine load. When the NTP charger was activated, the total particle mass concentrations were shown to reduce by the maximum values of 84.9\% for D100 and 83.2\% for WCO but increased in size for both fuels and loads. The total particle masses were higher for D100 for the two load conditions tested. During the NTP charger activation, the MMD was enlarged by 24.0\% maximum for D100 and 5.5\% maximum for WCO.

The PM removal efficiencies were maximized by 10.8\% for D100 and 16.7\% for WCO when the NTP charger was in use. When the NTP charger was activated, the WCO was dominantly seen to reduce \(\text{NO}_x\) and PM exhaust emission simultaneously compared to that of D100. The \(\text{NO}_x\) reduction is due to the dissociation of NO and NO\(_2\) molecules by electron collision in the discharge plasma through the plasma chemistry reactions in the presence of water.

Compared to other catalytic after-treatment systems, the main advantage of the NTP technique is beneficial on a superior internal pressure drop and power consumption. Engine optimizations for fuel injection strategies and exhaust gas recirculation (EGR) combined with a turbocharger would be the subject of further research study.

### EXPERIMENTAL SECTION

**Particle Source.** The source of particles was a diesel engine (Nissan, model TD27) that ran in steady-state load and speed conditions. The engine was water-cooled and four-stroke operated, with its main specification listed in Table 1. The engine was loaded by an eddy current type engine dynamometer (DYNOMite, model 012-200-1K) to continuously generate PM. The engine dynamometer test rig with its rudimentary instrument is illustrated in Figure 8.

**Fuel.** Two types of fuels were used in the test: biodiesel (WCO) and diesel (D100). Note that a subtle content of fatty acid methyl ester (FAME) was presented in the diesel fuel by local regulation. Fuel analyses for key properties of the test fuels obtained from a third-party laboratory are enumerated in Table 2.

### Table 1. Engine Specifications

| key parameters | specifications |
|----------------|---------------|
| engine type    | 4-stroke, in-line 4-cylinder |
| bore           | 96 mm         |
| stroke         | 92 mm         |
| displaced volume | 2663 cc |
| compression ratio | 22:1       |
| maximum torque | 180 N·m at 2200 rpm |
| maximum power  | 62 kW at 4300 rpm  |

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Particle Number Concentration and Size Measurements. The measurements of particle number and size were based on a partial flow system as shown in Figure 8. Being iso-kinetically drawn into a diluter at a constant 10:1 dilution ratio, the sampled exhaust gas was mixed with the oxygen diluent (Praxair, 99.7% purity). The diluted samples at a controlled constant flow rate were entered into a scanning mobility particle sizer (TSI, model NanoScan SMPS 3910), which can measure particles in the size range of $10^{-4}$ to $400$ nm. The other separated route for the diluted samples was directed to an optical particle sizer (TSI, model OPS 3330) that can measure particles in the size range of $300$ to $10000$ nm. Both results were merged by a Multi-Instrument Manager software from TSI. The exhaust gas samples were collected and averaged for 60 min; the averaged values are presented here as representatives. The subsequent particle number concentrations were later corrected for dilution and illustrated the engine’s nondiluted exhaust gas emission. The surface area was subsequently calculated on the assumption of an equivalently spherical shape of PM.

Exhaust Emission Measurement. On a dry basis, an exhaust gas analyzer (Horiba, model MEXA-584L) was used to measure the total unburned hydrocarbon (HC) and carbon monoxide (CO) while another analyzer (Testo, model 350-XL) was used to measure nitrogen oxides ($\text{NO}_x$). The working principle of both analyzers is based on a nondispersive infrared (NDIR) measurement. These emissions were volumetrically based and eventually converted to mass basis in the unit of g/kWh. The black smoke of the exhaust gas in opacity percentage was measured by a smoke meter (Horiba, model MEXA-600S) based on the light absorption. The measured smoke opacity was then converted to PM emission in g/kWh by calculation. The measuring range and accuracy of the exhaust gas analyzer and smoke meter are given in Table 3.

Nonthermal Plasma Charger. A reactor of nonthermal plasma (NTP) charger was placed downstream of an isokinetic drawing tube in the engine exhaust system as shown in Figure 8. A quartz tube section of the charger was situated in between a stainless steel exhaust pipe, as shown in Figure 9. The NTP charger system operated under an applied voltage of 25 kV and a repetition rate of 10 kHz. The system featured electrodes and a high-voltage pulse power supply to generate the flowing element into the nonthermal plasma state. The quartz tube was used as a dielectric barrier 50 mm in diameter and 600 mm in length. The electrical electrode set consisted of a core electrode and three spiral discharge electrodes. The spiral electrodes were equipped on an outer surface of the dielectric barrier. The NTP charger consumed input power from an ordinary 12 VDC battery, recharged by a regular alternator of the engine electrical system.

Table 2. Properties of the Test Fuels

| fuel analyses method | WCO | D100 |
|----------------------|-----|------|
| kinematic viscosity at 40 °C (cSt) | ASTM D445 | 4.5 | 2.9 |
| flash point (°C) | ASTM D93 | 142 | 60 |
| density at 15 °C (g/cm³) | ASTM D4052 | 0.8752 | 0.8255 |
| cetane number | ASTM D613 | 62.4 | 58.8 |
| lower calorific value (MJ/kg) | ASTM D240 | 39.9 | 42.5 |
| sulfur content (% wt) | ASTM D2622 | 0.003 | 0.0037 |
| ester content (% wt) | EN 14103 | 98.08 | 4.86 |
| oxidation stability at 110 °C (h) | EN 14112 | 6.85 | >10 |

Table 3. Exhaust Emission Measuring Accuracy and Range

| species | range | resolution | accuracy |
|---------|-------|------------|----------|
| CO      | 0–10% v/v | 0.01% v/v  | ±0.01% v/v |
| HC      | 0–10 000 ppm | 1 ppm | ±3.3 ppm |
| $\text{NO}_x$ | 0–3000 ppm | 1 ppm | ±5 ppm |
| PM      | 0–99.9% opac. | 0.1% opac. | ±0.5% opac. |
Test Conditions and Procedure. The engine was operated under steady-state conditions at 1500 rpm and became loaded at 2.5 and 4.0 bar brake mean effective pressure (BMEP). These two conditions at a relatively low speed are generally considered as medium and high loads intended to generate PM (low temperature, high fuel quantity injected). By fueling with WCO and D100, the engine was first fired and run to its normal hot condition as monitored by the coolant temperature (~90 °C). Thereafter, it was kept in steady-state conditions under the assumption of a uniform exhaust gas composition released. To eradicate the temperature effects on the PM result interpretation, all fuels were controlled for all of the tests to 40 ± 1 °C. All engine operating conditions were tested without engine recalibration.

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REFERENCES

1. Patiño, Y.; Fabá, L.; Díaz, E.; Ordoñez, S. Biodiesel production from wastewater sludge using exchange resins as heterogeneous acid catalyst: Catalyst selection and sludge pre-treatments. J. Water Process Eng. 2021, 44, No. 102335.
2. Wei, J.; Wang, Y. Effects of biodiesels on the physicochemical properties and oxidative reactivity of diesel particulates: A review. Sci. Total Environ. 2021, 788, No. 147753.
3. Wang, B.; Or, W.-H.; Lee, S.-C.; Leung, Y.-C.; Organ, B.; Ho, K.-F. Characteristics of particle emissions from light duty diesel vehicle fueled with ultralow sulphur diesel and biodiesel blend. Atmos. Pollut. Res. 2021, 12, No. 101169.
4. Abnisa, F.; Sanni, S. E.; Alaba, P. A. Comparative study of catalytic performance and degradation kinetics of biodiesels produced using heterogeneous catalysts from kaolinite. J. Environ. Chem. Eng. 2021, 9, No. 105569.
5. Gupta, J. G.; Agarwal, A. K. Engine durability and lubricating oil tribology study of a biodiesel fuelled common rail direct injection medium-duty transportation diesel engine. Wear 2021, 486–487, No. 204159.
6. Adenuga, A. A.; Oyekunle, J. A. O.; Idowu, O. O. Pathway to reduce free fatty acid formation in Calophyllum inophyllum kernel oil: A renewable feedstock for biodiesel production. J. Clean. Prod. 2021, 316, No. 128222.
7. Rattanapolee, P.; Duijanut, P.; Muannruska, P.; Kaewkannetra, P. Biocircular platform for third generation biodiesel production: Batch/ted batch mixotropic cultivations of microalgae using glycerol waste as a carbon source. Biochem. Eng. J. 2021, 175, No. 108128.
8. Dias, A. P. S.; Ramos, M.; Catarino, M.; Pereira, M. F. C. Biodiesel by co-processing animal fat/vegetable oil mixtures over basic heterogeneous Ca catalyst. Clean. Eng. Technol. 2020, 1, No. 100012.
9. Joubert, R.-L.; Jokonya, O. A systematic literature review of factors affecting the adoption of technologies in food waste management. Procedia Comput. Sci. 2021, 181, 1034–1040.
10. Elkelawy, M.; El Shenawy, E. A.; Almonem, S. K. A.; Nasef, M. H.; Panchal, H.; Bastawissi, H. A.-E.; Sadasivuni, K. K.; Choudhary, A. K.; Sharma, D.; Khalid, M. Experimental study on combustion, performance, and emission behaviours of diesel/WCO biodiesel/ Cyclohexane blends in DI-CI engine. Process Saf. Environ. Prot. 2021, 149, 684–697.
11. Hwang, J.; Bae, C.; Gupta, T. Application of waste cooking oil (WCO) biodiesel in a compression ignition engine. Fuel 2016, 176, 20–31.
12. Plamondon, E.; Seers, P. Parametric study of pilot−main injection strategies on the performance of a light-duty diesel engine fueled with diesel or a WCO biodiesel−diesel blend. Fuel 2019, 236, 1273−1281.
13. Tayari, S.; Abedi, R.; Rahi, A. Comparative assessment of engine performance and emissions fueled with three different biodiesel generations. Renewable Energy 2020, 147, 1058−1069.
14. Sahu, T. K.; Sarkar, S.; Shukla, P. C. Combustion investigation of waste cooking oil (WCO) with varying compression ratio in a single cylinder CI engine. Fuel 2021, 283, No. 119262.
15. Jung, Y.; Hwang, J.; Bae, C. Assessment of particulate matter in exhaust gas for biodiesel and diesel under conventional and low

https://pubs.acs.org/doi/10.1021/acsomega.1c06597

Notes

The authors declare no competing financial interest.
Exhaust Nonthermal Plasma Charger Using Thermo-gravimetric Analysis, SAE Technical Paper, 2015-01-0111, 2015.
(35) Kuroki, T.; Ishidate, M.; Okubo, M.; Yamamoto, T. Charge-to-mass ratio and dendrite structure of diesel particulate matter charged by corona discharge. Carbon 2010, 48, 184–190.
(36) Wongchang, T.; Sittichompoo, S.; Theinnoi, K.; Sawatmongkhon, B.; Jugai, S. Impact of high-voltage discharge after-treatment technology on diesel engine particulate matter composition and gaseous emissions. ACS Omega 2021, 6, 21181–21192.
(37) Penetrante, B. M.; Schultheis, S. E. Non-thermal Plasma Techniques for Pollution Control: Part B—Electron Beam and Electrical Discharge Processing; Springer Verlag: Berlin, 1993.
(38) Ma, C.; Gao, J.; Zhong, L.; Xing, S. Experimental investigation of the oxidation behaviour and thermal kinetics of diesel particulate matter with non-thermal plasma. Appl. Therm. Eng. 2016, 99, 1110–1118.
(39) Van Gulijk, C.; Schouten, J. M.; Marijnissen, J. C. M.; Meek, M.; Moulijn, J. A. Restriction for the ELPI in diesel particulate measurements. Aerosol Sci. 2001, 32, 1117–1130.
(40) Jolibois, J.; Takakshima, K.; Mizuno, A. Application of a non-thermal surface plasma discharge in wet condition for gas exhaust treatment: NO removal. J. Electrost. 2012, 70, 300–308.
(41) Talebizadeh, P.; Babaie, M.; Brown, R.; Rahimzadeh, H.; Ristovski, Z.; Araí, M. The role of non-thermal plasma technique in NO2 treatment: A review. Renewable Sustainable Energy Rev. 2014, 40, 886–901.
(42) Khacef, A.; Cormier, J. M.; Pouvèse, J. M. NOx remediation in oxygen-rich exhaust gas using atmospheric pressure non-thermal plasma generated by a pulsed nanosecond dielectric barrier discharge. J. Phys. D: Appl. Phys. 2002, 35, 1491–1498.
(43) Khani, M. R.; Pour, E. B.; Rashnoo, S.; Tu, X.; Ghobadian, B.; Shokri, B.; Khadem, A.; Hosseini, S. I. Real diesel engine exhaust emission control: indirect non-thermal plasma and comparison to direct plasma for NOx, THC, CO, and CO2. J. Environ. Health Sci. Eng. 2020, 18, 743–754.
(44) Talebizadeh, P.; Rahimzadeh, H.; Babaie, M.; Anghizhi, S. J.; Ghomi, H.; Akhmedi, G.; Brown, R. Evaluation of residence time on nitrogen oxides removal in non-thermal plasma reactor. PLoS One 2015, 10, No. e0140897.
(45) Yamamoto, T.; Okubo, M.; Hayakawa, K.; Kitsaura, K. Towards ideal NOx control technology using a plasma—chemical hybrid process. IEEE Trans. Ind. Appl. 2001, 37, 1492–1498.
(46) Vinh, T. Q.; Watanabe, S.; Furuhata, T.; Araí, M. Fundamental study of NOx removal from diesel exhaust gas by dielectric barrier discharge reactor. J. Mech. Sci. Technol. 2012, 26, 1921–1928.
(47) Wang, Y.; Wong, V.; Sappok, A.; Munnis, S. In The Sensitivity of DPF Performance to the Spatial Distribution of Ash Inside DPF Inlet Channels, SAE Technical Paper, 2013-01-1584, 2013.
(48) Sappok, A.; Wong, V. In Ash Effects on Diesel Particulate Filter Pressure Drop Sensitivity to Soot and Implications for Regeneration Frequency and DPF Control, SAE Technical Paper, 2010-01-0811, 2010.