Nanoparticle Components and Number–Size Distribution of Waste Cooking Oil-Based Biodiesel Exhaust Gas from a Diesel Particulate Filter-Equipped Engine

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ABSTRACT: An experimental study of the particulate matter (PM)-related emissions from the combustion of waste cooking oil (WCO)-based biodiesel-blended (0%, 30%, and 100% v/v) fuels in a four-cylinder diesel particulate filter (DPF)-equipped engine was carried out. A laboratory-scale DPF under the controlled conditions was installed into an aftertreatment system, and the PM mass and number characteristics were investigated. The combustion analysis based on in-cylinder pressure shows that the added WCO shortened the ignition delay, advanced the combustion ignition, and increased peak pressure values compared to conventional diesel fuel. The WCO increase in specific fuel consumption led to a slight reduction in brake thermal efficiency. The WCO-fueled engine showed reduced PM and total unburned hydrocarbon but increased nitric oxide emission. The nucleation and accumulation were characterized for nanoparticle number and size distribution. The particle number (PN) concentration in total was declined to smaller values when fueling with WCO. In the thermogravimetric analysis, the PM of WCO oxidized to a greater level than that of diesel fuel, which was observed by the weight loss rates during the specified heating program. WCO lowered the elemental carbon (EC) part of PM than diesel fuel. When equipping an exhaust system with DPF, the EC and the total PN drastically reduced while the particle size slightly increased. The use of DPF with the WCO biodiesel mitigated both EC and organic carbon components of the captured particles of the released PM.

INTRODUCTION

One of the main exhaust gases emitted from diesel engines is particulate matter (PM) that has been globally regulated by law. Various forms of PM can be seen as organic and inorganic compounds as a black smoke with nanosize composition or an even clear gaseous phase. When inhaled, organic particle pollutants are harmful to human lungs and health. Other greenhouse gases emitted from diesel combustion are also of concern in terms of causing atmospheric pollution. Much effort has been made to improve and endurably develop diesel engines for sustainability in various aspects, for example, renewable fuel, pollution reduction, energy consumption, and so forth.

Technologically, a number of alternative fuels for diesel vehicles have been trialed and investigated. Biodiesels are a promising renewable type of fuel in the forms of various esters depending on reactants, catalysts, or production techniques that suit to feedstock. Biodiesel has gained distinct attention for its renewability as well as potentiality in reducing well-to-wheel greenhouse gas emission, air pollution, and reliance on fossil fuel. By blending with diesel fuel to diverse extents, biodiesel can be directly used in standing diesel engines without recalibration. However, nitrogen oxide (NOx) emission may upsurge over tightened on-road emission legislations globally applied. In the meantime, a number of research protocols have been established to apply a volumetric blend of 30% biodiesel in conventional diesel fuel, commonly known as B30, toward achieving a greener diesel engine. Currently, producing a commercial biodiesel requires high cost. The key issue in general batch biodiesel production has been reported to be the feedstock cost as a food-grade virgin vegetable oil is commonly used. Using low-cost raw materials such as various types of used oil for the production can reduce the cost of biodiesel. This waste cooking oil (WCO) will be able to reduce the production cost by up to 70%. However, for its application in diesel engines, a large variety of WCO biodiesels from various origins has to be considered. More complicated production processes and
compliance to biodiesel standards for road diesel vehicles must be considered.9

In diesel engines, the combustion process is typically dealt with mixing-controlled (diffusion) combustion in majority, where high-temperature exposure and fuel-richness in the spray core region generate NOx and PM.10 A number of techniques have been explored to disrupt these trade-off emissions such as oxygenated fuel dosage, fuel injection strategies, combustion techniques, exhaust gas aftertreatment, and so on. Razak et al. (2021)11 optimized butanol blended to the diesel and biodiesel mixture that mainly reduced NOx emissions due to the fuel blend’s physicochemical properties. Butanol’s high heat of vaporization reduced the combustion temperature and hence suppressed NOx emission by up to 15%. Dimitriadis et al. (2020)12 improved PM–NOx trade-off by using hydrotreated vegetable oil with different fuel injection pressures as well as pilot and main injection timings. The significant reduction of NOx by 20% retarded the main injection timing by a 2° crank angle (CA), while PM was well below the respective diesel fuel level. Pan et al. (2019)13 integrated n-octanol augmentation and exhaust gas recirculation (EGR) to a diesel engine for concurrent NOx and PM reduction. Soot and particulates were well mitigated by the blended fuel of n-octanol and diesel incorporated with EGR. Jain et al. (2017)14 established the divided fuel injection and EGR strategy protocols for PM and NOx reduction in a low-temperature combustion (LTC) mode. The LTC program was accomplished by premixed charge compression ignition (PCCI) that was found to be superlative for the start of pilot injection at 35° before the top center and 15% EGR. In terms of aftertreatment devices, Cheng et al. (2017)15 developed a 3DOM CeO2-Mn3O4-ZrO2 catalyst that combined the selective catalytic reduction and particulate filter (SCRPF). This novel catalyst accommodated the maximum carbon dioxide concentration at 402 °C in burning PM and exhibited outstanding NH3-SCR performance in the range of 374–512 °C.

Diesel PM from combustion sources is a multifaceted compound of various carbons, ions, metals, and elements.16 Particles are varied in size, composition, solubility, and state that can change with surrounding conditions.17 PM is formed in the process of growth of precursor molecules from nanoparticles, which later coagulated into small particles that may collide and combine to form larger spherical particles. In its core, hardening causes the formation of fractal structures of carbon soot, whose atoms are bonded together in a hexagonal pattern, which are arranged in crystalline layers.18 This carbon core further absorbs hydrocarbons (HCs) and other compounds that turn into larger particles, and physiochemical properties of complex carbon soot eventually change. The enveloped HC components are the soluble organic fraction (SOF) commonly known as volatile organic compound (VOC) mainly arising from unburned fuel and lubrication oil contaminated during burning.19 An analytical technique such as thermogravimetric analysis (TGA) is usually used to determine PM stability, kinetic parameters, and volatile fractions.20 Subjected to a temperature ramp method inside a furnace in the air or an inert atmosphere, PM’s weight loss is continuously recorded and analyzed.21

With the advent of advanced technology arising from internal combustion engine development, many countries and regions have established particle number (PN) regulation protocols. PN concentration–size distribution has been used to physically characterize the PM characteristics. The PN characterization is beneficial in many aspects especially for advanced diesel engines that run on alternative fuels such as biodiesel. In a modern common rail diesel engine reported by Chuepeng et al. (2011),22 B30 was compared with ultralow sulfur diesel (ULSD) in terms of PN concentration–size distribution and total PN. Burning of B30 generated a greater PN concentration with a smaller size (nucleation mode, 5–50 nm in equivalent diameter) compared to ULSD, prominently shown in accumulation mode (50–1,000 nm in equivalent diameter), leading to a reduction in PM mass. Furthermore, Nabi et al. (2017)23 reported on using a six-cylinder common rail fuel-injected turbocharged diesel engine over the European Stationary Cycle (ESC). Both PM and PN emitted from the engine fueled by WCO-based biodiesel volumetric blends of 20, 40, and 60% were found to substantially reduce compared with fossil diesel fuel. Nabi et al. (2019)24 also assessed waste cooking biodiesel (WBD100), reference diesel (D100), and three biodiesel blends. The latter blends were proportioned by 70/30/0, 70/20/10, and 70/10/20 of D100/WBD100/diethylene glycol dimethyl ether. The three biodiesel blends and WBD100 drastically lowered PM and PN but had a drawback of NOx emissions. Recently, for a diesel bus, Zhang et al. (2019)25 evaluated the WCO biodiesel effects on PN size distribution as well as PM compositions such as polycyclic aromatic hydrocarbons (PAHs), organic carbon (OC), elemental carbon (EC), and so forth. The biodiesel increased the nucleation mode particles and EC but decreased the OC and PAH emissions.

To cope with increasingly stringent worldwide legislations for PM emission, a diesel particulate filter (DPF) has been crucially developed and incorporated with other required aftertreatment technologies.26 For diesel and gasoline engines in some classes that became into force, the Euro VI emission standard for light commercial vehicles not only reduces the particle mass but also reduces PN release.27 Controlling diesel PM and PN emissions is an issue requiring specified solutions in terms of fuels, engines, and aftertreatment industries. The DPF has been developed to be effective with more than 90% filtration efficiency with heat resistant property as well as acceptable mechanical and thermal durability.28 Designs of the filter are usually a wall-type flow monolith in a ceramic cylinder with many parallel tiny channels along with the axial direction.29 In a standard DPF, the diesel PM is contained within the filter compartment when its layers onset to stabilize in the monolithic channels.30 Although DPF will be effective in filtering PM in exhaust gas, clogging of PM inside the filter may also occur. Therefore, the DPF devices eventually require a regeneration process to extend their service life, both for standard and catalyzed DPFs.31 In the transient computational fluid dynamics-based simulation in a single-channel configuration, the uniform soot load substantially combusted under controlled temperature conditions in a catalytic DPF.32 Recently, a high-performance Ceria-coated DPF was developed for continuous regeneration.33 Its catalytic oxidation of soot starts from 300 °C, and the conversion of soot to carbon dioxide was higher than 99% in the temperature range of 200–600 °C.

From the literature review, most of the studies described about biodiesels produced using various sources and their effect on engine performance and exhaust gas emissions. Meanwhile, limited work has been carried out on the role of biodiesel in DPF’s performance.34 Additionally, a neat WCO-based biodiesel or a blend may be suitable to be used as a fuel
for a DPF-equipped engine for reducing PM or impurities during regeneration.\textsuperscript{35,36} Besides, there is less available information on the OC and EC components as well as the nanoparticle number-size distribution in a DPF-equipped engine fueled by WCO-based biodiesel. Subsequently, some other aspects of these issues have not yet been discussed.

This study aims to investigate the effects of WCO biodiesel blend (WCO30) combustion in a wall-type DPF-equipped diesel engine on PM components and nanoparticle number distribution. The engine was experimentally run by neat diesel (D100) and biodiesel (WCO100) for comparison under low and medium loads at a constant speed of 2500 rpm. The engine performance in terms of specific fuel consumption and thermal efficiency as well as engine combustion characteristics such as ignition delay, combustion duration, and peak cylinder pressure will be first explored as they are the causes of the exhaust gas emissions. The PM-related mass, number, and smoke opacity were also investigated in parallel. The details of the PM components (OC and EC) investigated by TGA and nanoparticle number distribution examined using an optical particle sizer in conjunction with a scanning mobility particle sizer were presented and discussed in combination with DPF’s performance.

\section*{RESULTS AND DISCUSSION}

\textbf{Combustion Parameters and Efficiency.} The combustion characteristics of D100, WCO30, and WCO100 in an unmodified compression ignition (CI) engine are first shown in Figure 1 for average peak cylinder pressures of 1.5 bar and 3.5 bar and a brake mean effective pressure (BMEP) load of 2500 rpm. The experimental data for peak cylinder pressure slightly increase with the WCO proportion. The average peak pressures were 57.9, 58.2, and 58.3 bar for a low load, and 58.4, 58.8, and 58.9 bar for a medium load of D100, WCO30, and WCO100, respectively. The main cause for the increase of peak cylinder pressure in the CI engine with WCO biodiesel is the increased amount of oxygen in the fuel resulting in a higher peak pressure that improves the combustion process by entraining the oxidizer into the local fuel-rich sprayed core. This phenomenon was also reported by Zare et al. (2017).\textsuperscript{37}

![Figure 1. Average peak pressure.](image)

The increasing WCO proportions shortened the ignition delay as shown in Figure 2. The ignition delays of different blended fuels and engine loads were 19.8, 17.9, and 17.1° CA for a low load, and 18.1, 16.3, and 15.7° CA for a medium load of D100, WCO30, and WCO100, respectively. The increasing WCO proportions, which reduce the ignition delay, advanced the start of combustion to earlier CA positions, related to the peak pressures increasing over the D100 combustion. These trends of results are in line with those findings reported in Chuepeng and Komintarachat (2018).\textsuperscript{10} Several physical properties of the neat WCO biodiesel such as bulk modulus, density, and viscosity are attributed to a complex and rapid chemical reaction taking place at a high temperature in preflame.\textsuperscript{38} The subsequent cylinder temperature existing during biodiesel fuel injection causes thermal cracking, which might have ignited earlier. Furthermore, the cetane number of the WCO biodiesel is higher than that of ordinary D100 that is a cause for the early ignition.

![Figure 2. Ignition delay and the combustion duration.](image)

Figure 2 also shows the combustion durations of different blended fuels that were lengthened by increasing WCO biodiesel proportions. The combustion durations were 27.8, 29.9, and 30.7° CA for a low load, and 33.9, 35.7, and 36.1° CA for a medium load of D100, WCO30, and WCO100, respectively. For all fuels, the combustion duration increased with increasing engine load. This can be explained by the fact that, at a higher load, the engine doses more fuel into the combustion chamber that requires a longer time to terminate burning. Atomization of the fuels was affected by viscosity and surface tension. WCO100 with a higher viscosity burned for a longer duration than D100. WCO100 with a higher surface tension offers resistance to fuel atomization. This lengthens the time for the fuel to burn in the engine cylinder.

Figure 3 illustrates the brake thermal efficiency (BTE) and BSFC for all fuel types. In general, the BSFC decreased with increasing engine load. The conversion of chemical energy in the fuel seems to be efficient at a higher load, where the brake power output at the engine’s crankshaft shows a greater effect than the fuel consumption. Upon increasing the ratio of the WCO biodiesel, its BSFC becomes higher than that of the diesel fuel under the same conditions. It was found that when compared with the D100 fuel, the rate of BSFC was increased...
by 11.5 and 16.1% for WCO30 and WCO100, respectively, at 1.5 bar BMEP, and 3.1 and 11.2% for WCO30 and WCO100, respectively, at 3.5 bar BMEP. These phenomena inherently occur by the decrement of the heating value of WCO100, which was also reported by Tesfa et al. (2013). Therefore, the fuel mass used for WCO-contained fuels would increase to maintain the set load. The BSFC values affect the BTE as shown in Figure 3. The BTE is described by the actual engine brake work divided by the energy input to an engine. The BTE values obtained from the experiment were 23.3, 20.9, and 20.1% for D100, WCO30, and WCO100, respectively, at 1.5 bar BMEP, and 31.7, 30.8, and 28.5% for D100, WCO30, and WCO100, respectively, at 3.5 bar BMEP. When the engine was running under the same test conditions, the BTE values of WCO-contained fuels were lower in comparison with that of the D100 fuel. Higher viscosity of the fuel leads to reduced fuel atomization and vaporization, resulting in a lower value of BTE of the biodiesel. Moreover, from the combustion findings, the WCO biodiesel has an enhanced peak combustion pressure and an extended combustion duration, which may be related to the reduction in BTE. Heat losses to the combustion chamber walls are increased by the extended combustion duration and strengthened burning. Hence it can result in a lower fuel conversion efficiency, and a relatively lower BTE with increasing combustion duration.

**Exhaust Gas Emissions.** HC emission is derived from incomplete combustion of the fuel and oils under different engine design and operating conditions. In the combustion chamber of a diesel engine, local fuel-rich zones slow down the chemical reaction and cool the flame to quench. In addition, a longer ignition delay period results in an increase in HC emission. Figure 4 shows the amounts of HC at 1.5 bar and 3.5 bar BMEP loads, which are engine-out conditions for all fuels. The amounts of HC were the highest at 1.5 BMEP for all fuel types. This lower load has a lower temperature in the combustion chamber that causes HC deposition over the cylinder liner with some entrainment into the exhaust gas. The combustion of WCO-contained fuels tended to reduce HC with a greater effect for a higher proportion of the WCO biodiesel. The quantities of HC were 1.922, 1.488, and 1.141 g/kW h for D100, WCO30, and WCO100, respectively, at 1.5 bar BMEP, and 0.677, 0.594, and 0.544 g/kW h for D100, WCO30, and WCO100, respectively, at 3.5 bar BMEP. The oxygen content of the biodiesel partly present in the fuel contributes to improved fuel oxidation resulting in cleaner engine combustion and the reduction in HC emission. This trend is in agreement with that reported by Özener et al. (2014).

The exhaust emissions under engine-out conditions of NO and PM are depicted in Figure 5. Under each condition, the PM was decreased when the proportions of the WCO biodiesel increased, but the NO emission shows a reverse effect as a trade-off. The amounts of NO were 3.002, 3.181, and 3.293 g/kW h for D100, WCO30, and WCO100, respectively, at 1.5 bar BMEP, and 1.761, 2.033, and 2.122 g/kW h for D100, WCO30, and WCO100, respectively, at 3.5 bar BMEP. The increasing proportions of the WCO biodiesel in the fuels resulted in the increasing NO emission. The increasing NO concentration in the exhaust gas during WCO-contained fueling can be caused by high temperature exposure of the combustion gas that contains a greater level of oxygen, generating more complete combustion. Also, superfluous oxygen in the fuels themselves prolongs the combustion duration, providing more times for NO formation. Diesel engines release a significant quantity of NO, where its...
formation is governed by the well-known Zeldovich mechanism that deals with temperature and the oxygen concentration. The obtained results are different from those reported by Chuepeng et al. (2011)22 that the NO concentration in the exhaust gas during rapeseed-based biodiesel fueling was reduced. The main reason for efficient reduction of NO emission while fueling by biodiesel was EGR and fuel injection strategies. The split injections into six events per cycle diminished the hot gas exposure for a long period of time and hence lower NO emission.

The masses of PM are also shown in Figure 5 for D100, WCO30, and WCO100 at 1.5 bar and 3.5 bar BMEP. A high mass is generally caused by incomplete combustion during the combustion of a rich mixture in the combustion chamber or insufficient oxygen during a high engine load. The PM masses were 0.764, 0.665, and 0.645 g/kW h for D100, WCO30, and WCO100, respectively, at 1.5 bar BMEP, and 0.628, 0.589, and 0.586 g/kW h for D100, WCO30, and WCO100, respectively, at 3.5 bar BMEP. The presence of oxygen in the WCO biodiesel improved the oxidation inside locally rich fuel combustion zones, especially in the PM-forming region at the core of the spray. Furthermore, increased availability of oxygen during combustion of biodiesel in the part of premixed reaction zones leads to a better combustion, affecting the reduction rate of the PM formation reactions.22

Compared to the PM trends reported in Chuepeng et al. (2011),22 the obtained results from this experiment are agreed in terms of engine loads (low and medium loads). In addition, the quantitative impact of biodiesel portions in the blended fuels (B30 vs WCO30) is also similar even to different biodiesel-based fuels (rapeseed oil vs WCO).

Figure 6 shows the PM masses in the exhaust gases after passing through the DPF at 1.5 bar and 3.5 bar BMEP for all fuels, and shows a comparison of the quantity of PM between the engine-out and with-DPF gases. It was found that the amount of PM reduces after passing through the DPF under all conditions of the experiment. The results of PM were reduced by 15.3, 12.9, and 10.4% for D100, WCO30, and WCO100, respectively, at 1.5 bar BMEP, and 25.2, 25.0, and 24.7% for D100, WCO30, and WCO100, respectively, at 3.5 bar BMEP. The DPF filtered the PM emission, which was drastically reduced for the flow passing through the DPF especially for D100 at a higher load.

**PN Distribution.** The PN concentrations in the lognormal distribution over the range of equivalent particle diameter in the exhaust gases from the engine fueled with D100, WCO30, and WCO100 were measured and are shown in Figures 7 and 8, respectively, for 1.5 and 3.5 bar BMEP loads, and at 2500 rpm in comparison between engine-out and with-DPF conditions. The results show that the engine operating conditions affect the PN concentration-size distribution. The combustion of all fuels at the lower loads generates a lower PN concentration with a larger size, but a higher PN concentration with a smaller size at the higher loads. The maximum PN concentrations under the engine-out condition for all fuels are in the range of $6.86 \times 10^{-4}$ to $1.26 \times 10^{-2}$ $1/cm^3$ and $1.31 \times 10^{-4}$ to $2.95 \times 10^{-2} 1/cm^3$ for 1.5 bar and 3.5 bar BMEP loads, respectively. From the results obtained, both the engine load and speed conditions generate the PN concentration in nucleation and accumulation modes. When the engine load increased, the PN concentration increased. It may be caused by more fuel additionally injected into the cylinder, where the air-to-fuel ratio decreased but the combustion period lengthened.

Figures 7 and 8 also show the PN concentration-size distribution after the exhaust gas passing through the DPF (the with-DPF condition). In the DPF, the PN burned at elevated temperatures and pressures promotes the growth of nucleation mode and hence a smaller particle size and a greater PN concentration. It is found that the WCO biodiesel reduced the PN concentration and particle size after passing through the DPF. From the experiment regardless of fuels used, the maximum PN concentrations were in the ranges of $5.94 \times 10^{-4}$ to $7.75 \times 10^{-4} 1/cm^3$ and $1.55 \times 10^{-4}$ to $3.09 \times 10^{-4} 1/cm^3$ for 1.5 bar and 3.5 bar BMEP loads, respectively. The particle diameters after passing through DPF approximately range from 81.0 to 92.7 nm and 70.8 to 86.7 nm for 1.5 bar and 3.5 bar BMEP loads, respectively.

Figure 9 shows the total PN concentrations versus count mean diameter when fueling the engine by D100, WCO30, and WCO100 at 1.5 and 3.5 bar BMEP loads, and at 2500 rpm in comparison between engine-out and with-DPF conditions. It was found that the engine operating conditions affected the count mean diameter of the particle in average. The amounts of total PN concentration in the exhaust gas were in the range of $1.38 \times 10^{-4}$ to $2.38 \times 10^{-4} 1/cm^3$ and $2.07 \times 10^{-4}$ to $5.27 \times 10^{-4} 1/cm^3$ for 1.5 bar and 3.5 bar BMEP loads, respectively. The average count mean diameters for the particles under the engine-out condition approximately range from 87.4 to 91.3 nm and 69.0 to 82.4 nm for 1.5 bar and 3.5 bar BMEP loads, respectively. When comparing the PN concentration among fuels, it was found that increasing the WCO ratio reduced the PN concentrations, which led to smaller sizes of the burnt PM. Therefore, adding biodiesel into diesel fuel can lower the PN concentration compared to conventional diesel. These phenomena can be mainly explained by two factors: oxygen and aromatic contents in the fuel. The oxygen content in biodiesel can improve combustion in a more efficient manner, even in the area of combustion of a fuel-rich fuel mixture, and promote the oxidation of the generated particles.34 In addition, adding biodiesel reduces the level of aromatics, a precursor of soot formation from oxidized fuel droplets, especially for a higher engine load.21 As a result, the rate of soot formation is lower and the total PM number concentration is reduced. The
trends of results are in parallel to those obtained from a high fuel injection pressure system used in a common rail diesel engine. Figure 9 also shows that the DPF can filter the PM; the average total PN concentration reduced and the count mean diameter reduced to smaller sizes. For the exhaust gases after passing through the DPF, the average total PN concentrations were $9.74 \times 10^5$ to $1.67 \times 10^6$ 1/cm$^3$ and $2.38 \times 10^6$ to $4.83 \times 10^6$ 1/cm$^3$ for 1.5 bar and 3.5 bar BMEP loads, respectively. The average count mean diameters for the particles after passing through DPF approximately range from 90.7 to 94.0 nm and 75.4 to 85.8 nm for 1.5 bar and 3.5 bar BMEP loads, respectively. It can be seen from the obtained results that the filtration affected the accumulation mode rather than the nucleation mode. The filter not only reduces the PN concentrations for a specific size range but also changes the distribution shape and peak diameter. However, the peak diameter becoming larger can be caused by the particle growth through condensation and coagulation while passing through
the DPF, where a high filter efficiency in removing the smaller PM from the exhaust occurs.21

**Thermogravimetric Analysis of PM Components.**

Thermogravimetric analysis (TGA) has been widely used to evaluate the thermal stability of various types of materials. The weight loss of PM samples is displayed in the form of particle mass fraction that may reduce depending on their characteristics when the samples are heated. Figures 10 and 11 show the weight losses of the PM samples expressed in terms of mass fractions that were reduced over TGA temperature under the engine conditions of 1.5 bar and 3.5 bar BMEP, respectively. In comparison, different mixture ratios of WCO result in different components of the PM under engine-out and with-DPF conditions. The mass loss curve for each mode decreased, at around 50−500 °C in a nitrogen environment, which is mainly caused by the loss of the volatile substances and the oxidation of the non-volatile substances, respectively. In addition, the remaining mass after this process is EC. The chemical reaction was completed at a temperature lower than the set temperature. Some fractions of the volatile material may be desorbing from the outer surface of carbon soot at a temperature higher than the boiling point. It was found that the particle mass fraction during continuous heating reduced before 500 °C with the different maximum rates from high to low of the order of WCO100 > WCO30 > D100 for all engine conditions. At the same temperature, the particle mass fraction of the WCO-contained fuels was lower than that of D100. This can be explained as that the PM of biodiesel comprises unburned oxygenated HC; acceleration of the oxidation process was achieved. Furthermore, after passing through DPF, the PM mass fraction even decreased to a greater extent compared to the engine-out condition.

Figures 12 and 13 show the PM mass fraction under 1.5 bar and 3.5 bar BMEP loads, respectively, for all fuels running under engine-out and with-DPF conditions. During heating, the samples undergo the presented temperature ramp program, volatile material or organic carbon (OC) was gathered in the temperature range of 50−500 °C but separated into two steps of temperature ranges. The volatile material, $V_1$, was obtained in the range of 50−200 °C, where moisture was vaporized, while the volatile material, $V_2$, was obtained in the temperature range of 200−500 °C, where unburned HCs were oxidized. Finally, the solid EC was obtained at temperatures higher than 500 °C. Therefore, at temperatures below 500 °C, weight loss from vaporization and devolatilization can be observed, while above 500 °C weight loss was caused by combustion. For all engine conditions and fuels, the OC portion under the engine-out condition was found to be increased when the ratio of
WCO increased. Regardless of the fuel type used, the volatile OC fraction was the highest under low load conditions when the exhaust gas was released at low temperatures. These phenomena were similar to those reported by Chuepeng et al. (2011). In the elevated high-temperature zone (over 500 °C in an oxygen environment) of the TGA, a residual mass or EC was also analyzed and the results are shown in Figures 12 and 13. In general, the EC levels have been found to be greater when increasing the engine load. It was found that increasing the WCO percentage in the fuel mixture lowered the EC part of the PM. The WCO100 particulates were lower for EC under both engine-out and after DPF conditions. When comparing the solid EC under the same conditions, the DPF can reduce the amount of EC under all operating conditions for all fuel types. For the same load under the engine-out conditions, it can be seen that D100 brought about the EC part higher than WCO. The combustion of WCO appears to produce larger amounts of OC that is attributed to the drastic reduction of PM regarding the more complete combustion for WCO previously observed. The obtained results resembled those reported in the literature based on other biodiesel types and test conditions. The method of TGA obviously shows the superior performance of DPF in trapping PM for WCO30 and WCO100, compared to D100. The practical benefits are highlighted for the use of the WCO biodiesel in terms of combustion and the relevant exhaust gas emission. The PM’s EC portion as well as PM mass and number are drastically reduced. Also, the WCO biodiesel’s PM can eventually be treated using the current DPF. Meanwhile, thermal efficiency can be further improved and NO emission can be further reduced by incorporation of advanced fuel injection control strategies and EGR. These would be viable and foreseeable for practical use upon continuous development of the technology.

### CONCLUSIONS

This study presents the analysis of the PM composition and related emissions in the combustion process of a diesel engine running on WCO-contained fuels (WCO30 and WCO100) in comparison with the D100 fuel. The experiments were conducted under low and medium loads of 1.5 bar and 3.5 bar BMEP, respectively, at 2500 rpm, and the exhaust samples were collected under the engine-out and with-DPF conditions.

The WCO biodiesel portion added to D100 and neat WCO biodiesel shortened the ignition delay and increased the peak pressure values compared to the D100 combustion. The BSFC was higher for WCO100 compared to WCO30 and D100 due to the specific energy of the fuel. As a result, the BTE was declined for WCO100 compared to D100 with that for WCO30 in between.

The exhaust emissions of HC and PM were found to decline to a greater extent under all loads tested for the engine running on the fuel containing the WCO biodiesel. The oxygen content of biodiesel presented in the fuel contributes to improved fuel oxidation at a higher combustion temperature resulting in a higher concentration of nitric oxide from WCO100 and WCO30 combustions. The oxygen in the biodiesel itself lengthened the combustion duration that stimulates an additional time for NO formation.

The analysis of the PN concentration over the range of equivalent particle diameter evidently displayed nucleation and accumulation modes on the logarithmic normal scale for all fuel types. When the mixture ratio of WCO biodiesel increased, the PN concentration and size reduced under all load conditions. Both the PM mass and number of the emissions after passing through DPF extremely reduced but the particle size slightly increased. The particle growth via condensation and coagulation was observed during exhaust flow through the DPF.

In the TGA, the mass change rates of OC and EC parts of the PM were obtained. WCO biodiesel’s PM oxidation at different rates depends on its incremental portion in the fuel. The PM formation during the combustion of WCO100 shows a lesser EC compared to D100 combustion. The EC can be trapped in the DPF and the PM was extremely reduced by WCO100 fueling. However, the OC part of the PM from WCO100 combustion was greater in amount but it can be later burned in the DPF.

From the combustion and emission parameters as well as PM and PN characteristics of the WCO biodiesel, synthesis and optimization of DPF catalysts that suit to the preparation of novel alternative fuels are crucially required. This should be accomplished in combination for advanced engine control strategies and other exhaust gas aftertreatment systems to conform with increasingly stringent emission legislations. These would be recommended for future research studies.

### EXPERIMENTAL SECTION

**PM Source.** The experimental study was carried out using a water-cooled diesel engine (Mitsubishi, model 4D56). The key engine specifications are specified in Table 1. The engine was installed in the test cell as depicted in Figure 14 and was fully equipped with rudimentary instrumentation described in the following sections.

**Table 1. Engine Specification**

| properties          | specifications          |
|---------------------|-------------------------|
| engine type         | in-line 4-cylinder      |
| bore × stroke       | 91.1 mm × 95.0 mm       |
| displaced volume    | 2476 cc                 |
| compression ratio   | 21:1                    |
| maximum torque      | 142 Nm at 2500 rpm      |
| maximum power       | 55 kW at 4200 rpm       |

**Test Rig Equipment.** An eddy current dynamometer (DYNOnitme, model 012-200-1K) was connected to the engine accompanied by a data acquisition system (National Instruments, model USB-6218) to log for local temperature and pressure based on the LabVIEW code. A balance (CST, model CDR-3) and a flow meter (Testo, model 435), which run with an accuracy of ±0.05 g and ±0.3% of reading, were used to measure fuel and air flow rates, respectively.

**DPF Configuration.** The DPF used in this experiment was a silicon-carbide type with a diameter of 25 mm and a length of 180 mm. The DPF was placed in an electrical furnace controlling the temperature in the range of 250 ± 15 °C (see Figure 14) to maintain the exhaust temperature over 180 °C. At a steady flow rate, the exhaust gas emissions were partially drawn by isokinetic sampling into a stainless steel located in the exhaust pipe, passing through the DPF. The samples gas was collected for emission analysis under engine-out and with-DPF conditions at the same engine operation points.

**Fuels.** Two types of neat fuels, conventional diesel and the WCO biodiesel, were used as base fuels for the blends. Three
Table 2. Elementary Fuel Properties

| Fuel Analysis     | D100  | WCO30 | WCO100 |
|-------------------|-------|-------|--------|
| Flash Point (°C)  | 70    | 78    | 142    |
| Density (g/cm³)   | 0.81  | 0.83  | 0.86   |
| LHV (MJ/kg)       | 45.2  | 43.8  | 39.9   |
| Water Content (ppm)| 77.5  | 274.6 | 1060.7 |
| Oxidation Stability (h) at 110 °C | 30.88 | 14.5  | 6.85   |

Combustion Parameter Measurement. The combustion characteristics were studied through the crankshaft position–indicated cylinder pressure data. The cylinder pressure traces were examined using a commercial software package (DEWEtool V6.6.9) based on the first law of thermodynamics. With a sensitivity of −19.90 pC/bar at 200 °C, a transducer (Kistler, model 6052C) measured the combustion pressures in the engine cylinder within ±0.4% FSO linearity. Later, a charge amplifier (DEWEtool, model DEWE-30-4) magnified and filtered the signal from the pressure transducer. In the meantime, the crankshaft position was indicated by a shaft encoder (Baumer Electric, model BDK 16.05A360-5-4) at 360 pulses per revolution sampling rate. At a 1 MS/s sampling rate, the triggered signals were then directed to a data acquisition system (DEWEtool, model DEWE-ORION-0816-100x). Hundred consecutive cycles of cylinder pressure traces were averaged and shown as representative for each single condition.

Measurement of Exhaust Gas Release. After moisture was removed, the pollutant emissions were analyzed using an exhaust gas analyzer (Horiba, Model MEXA-584L). The analyzer was accurately measured by 1.7% of reading in the range of 0–10,000 ppm for total unburned HC and 4% of reading in the range of 0–4,000 ppm for NO, the main constituent of NOₓ. A smoke meter (Motorscan, model 9010) measured the exhaust gas opacity percentage, which was converted to PM in g/kW h.

TGA. The PM samples of exhaust gas were filtered through uncoated glass microfiber filter papers (Whatman, model GF/C) at a constant volume flow rate. To avoid volatile material evaporation after collection, the samples kept in sealed containers were stored in a refrigerator. The PM samples from the engine were investigated using a thermogravimetric analyzer (PerkinElmer, Model Pyris 1 TGA) to evaluate their compositions. The analyzer has 2 °C precision, 0.1 μg sensitivity, and 0.02% accuracy of the balance. The samples were treated according to the heating program shown in Table 3.

Table 3. Heating Program for TGA

| Step     | Heating Program                      |
|----------|--------------------------------------|
| I        | Constant ambient temperature in N₂ for 10 min |
| II       | Ramping for the rate of 15 °C/min in N₂ to 500 °C |
| III      | Constant temperature of 500 °C in N₂ for 15 min |
| IV       | Constant temperature in air for 15 min |

PN–Size Distribution Determination. The PN distribution was compared between engine-out and with-DPF conditions based on a partial flow dilution. By isokinetically drawing into a 10:1 diluter, the sampled gas was entrained by the oxygen diluent (Praxair, 99.7% purity). The ratio of dilution was chosen in such a way to ensure that it was low enough and did not affect exhaust gas oxidation. In the meantime, the exhaust gas dilution was required for condensation and freezing of particles. At the flow rates of 0.95 and 0.65 L/min, the diluted samples were drawn to an optical particle sizer (OPS, TSI model OPS 3330) and a scanning mobility particle sizer (SMPS, TSI model NanoScan SMPS 3910), respectively. The SMPS and OPS can analyze PN in the size ranges of 10 to 400 nm and 300 to 10,000 nm, respectively. The exhaust gas sample under each condition was collected for 60 s and the average values were representative and are shown in the following sections. The PN concentration after the dilution was already corrected and is illustrated here as a non-diluted exhaust gas emission.

Operating Conditions Tested. The engine was examined at 2500 rpm at which the engine torque is maximized and delivered (see Table 1). Exhaust PM was generated when the engine was loaded at 1.5 and 3.5 bar BMEP; these two conditions are generally considered as low and medium loads delivered (see Table 1). Exhaust PM was generated when the engine was loaded at 1.5 and 3.5 bar BMEP; these two conditions are generally considered as low and medium loads.
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Notes
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Nomenclature
B30, 30% biodiesel blended with 70% diesel (by volume)
BMEP, brake mean effective pressure
BSFC, brake specific fuel consumption
BTE, brake thermal efficiency
CA, crank angle
CI, compression ignition
D100, neat diesel fuel
DPF, diesel particulate filter
EC, elemental carbon
EGR, exhaust gas recirculation
ESC, european stationary cycle
FSO, full scale output
HC, total unburned hydrocarbon
HVO, hydrotreated vegetable oil
LTC, low-temperature combustion
NOx, nitric oxide
NOE, nitrogen oxides
OC, organic carbon
OPS, optical particle sizer
PAHs, polycyclic aromatic hydrocarbons
PCCI, premixed charge compression ignition
PM, particulate matter
PN, particle number
ppm, part per million
SCRPF, selective catalytic reduction and particulate filter
SMPS, scanning mobility particle sizer
SOF, soluble organic fraction
TGA, thermogravimetric analysis
ULSD, ultralow sulfur diesel
VOC, volatile organic compound
WBD100, waste cooking biodiesel
WCO, waste cooking oil
WCO100, neat waste cooking oil
WCO30, 30% WCO blended with 70% diesel (by volume)

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