# EC/OC and PAHs Emissions from a Modern Diesel Engine with DPF Regeneration Fueled by 10% RME Biodiesel

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## ABSTRACT

In this study, the effect of using a blended biodiesel fuel containing 10% rapeseed methyl ester (RME) on the composition and quantity of the chemicals emitted by a modern diesel engine was investigated. The diesel engine that was utilized fulfilled Japan's Post New Long Term emission standards and was equipped with an after-treatment system comprising a diesel oxidation catalyst and a catalyzed diesel particulate filter (c-DPF). Using the Japanese JE05 transient cycle as the testing cycle, the exhaust gas was sampled for three different states: when the after-treatment system was not deployed, termed "engine-out" (due to the sampling location); when the after-treatment system was deployed, termed "tailpipe-out" (likewise due the sampling location); and when the after-treatment system was deployed and the c-DPF was regenerating, termed "regen". Evidence from this study indicated that the use of 10% RME biodiesel had no significant impact on the emissions of CO, $CO_2$, the total hydrocarbons, and $NO_x$, which are regulated, regardless of the sampling state. However, the emissions of elemental carbon, organic carbon, and polycyclic aromatic hydrocarbons (PAHs), which are unregulated, showed some effects. During engine-out and tailpipe-out, emissions of the elemental carbon species EC2 were slightly lower when using the biodiesel blend than the petroleum diesel (D) fuel; however, an increase in the organic carbon species OC1 and OC2 and in some PAHs was observed during regen because of the sizable consumption of the biodiesel blend compared to D fuel. These results confirm that 10% RME biodiesel is a promising alternative to fossil fuels for diesel engines, but it is important to grasp the behavior of individual components and carefully investigate the effects of increased mixing ratios.

*Keywords:* Particle composition; Engine-out; Tailpipe-out; Thermal desorption gas chromatography-mass spectrometry.

## INTRODUCTION

Biodiesel is regarded as an alternative to fossil fuels for powering compression ignition (CI) engines because this type of fuel is renewable, carbon-neutral, and biodegradable. Biodiesel is almost entirely made from edible vegetable oils (e.g., soybean, palm, and sunflower oils), and plant seed oils (e.g., rapeseed and linseed oils). Research focusing on biodiesel and aimed at addressing the air pollution and global warming resulting from the use of fossil fuels is actively being pursued around the world. Additional characteristics that render biodiesel appealing from a research and environmental standpoint are that it has a narrower boiling range than petroleum diesel (D) fuel, as well as a higher viscosity and cetane number, in conjunction with a lower volatility (Zheng *et al.*, 2006; He *et al.*, 2016). Reports published over the past few years indicate that the volume-based ranking of vegetable oil is as follows: soybean oil is the most widely produced vegetable oil, followed by palm oil and then rapeseed. Because of higher productivity per area and lower production cost, palm oil is one of the most appealing raw materials for biodiesel production. Soybean oil methyl ester is currently commercially available in the United States, whereas rapeseed methyl ester (RME) is available in some European countries (Kinoshita *et al.*, 2006). In Europe, biodiesel is mostly manufactured to meet the requirements (He *et al.*, 2016).

Given that, in general, at a molecular level biodiesel contains more oxygen atoms than D fuel, biodiesel-associated $NO_x$ emissions can also be higher than D fuel's emissions (Babu *et al.*, 2003; Sze *et al.*, 2007; Robbins *et al.*, 2011). Zhong *et al.* found that the ignition delay decreased with the increasing blending ratio of second-generation biodiesel (SGB), such as non-edible feedstocks, waste or recycle oils, and animal fats, as cetane number is an important factor for affecting the ignition delay. They concluded that when

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SGB blends in fuel, it reduces NO$_x$; however, the use of SGB can weaken the trade-off relation between particulate matter (PM) and NO$_x$. This is thought to be an advantage to solve the problems related to first-generation biodiesel.

Most of the studies concentrating on emissions originating from CI engines powered by biodiesel focused on regulated pollutants, such as particulate matter (PM), total hydrocarbons (THC), NO$_x$, and CO (Zhang *et al.*, 2011). The size of PM is also an important factor for affecting human health. Peters *et al.* (1997) conducted a short-term research on epidemiology. Their results indicated that size distribution of ambient particles helps to elucidate the properties of ambient aerosols responsible for the effects on human health. Chien *et al.* (2009) measured the size distribution of PM and PAHs. Furthermore, they indicated that for most biodiesel blending mixtures in four size ranges, the percentages of PAH emission reduction were higher than those of PM emission. Ajtai *et al.* (2016) reported that the ratio of biodiesel to petroleum diesel in the total fuel blend can influence both the total number and volume concentration and distribution of the particle emission. The total number and volume concentration emitted by the diesel engine decreased with increasing revolutions per minute and rated torque for the engine for all fuel blend types. Their observations revealed that the extent of the biodiesel content in the total fuel amount can influence the total volume and number of emitted particulates.

Over the past few years, furthermore, some researchers have focused attention on the effect that biodiesel fuels with different structures have on the effectiveness of exhaust after-treatment systems. Development of biodiesel fuels can be a powerful tool to further reduce the diesel exhaust gas and particle emissions and to fulfill the requirement of the continuously changing strict emission standards of the world. From the viewpoint of health effects, it is necessary to evaluate the emission inventory and future emission projection of diesel and biodiesel-powered vehicles, including the regeneration of DPF. However, literature focusing on the influence that active regeneration by diesel particulate filter (DPF) has on the chemical components of PM emitted by an engine operating on biodiesel fuel is very scarce.

This present study concentrates on evaluating the emissions of carbonaceous components and particle-phase polycyclic aromatic hydrocarbons (PAHs) with a diesel engine powered by either a 10% RME biodiesel blend or a D fuel. In particular, three engine operating conditions were utilized in our research: without the after-treatment system, termed "engine-out"; with the after-treatment system,

termed "tailpipe-out"; and during the active regeneration of the catalyzed diesel particulate filter (c-DPF), termed "regen," under the Japanese JE05 transient test cycle. This research is useful for finding the best countermeasure, such as adding a heat generation improver, for example, an electrically heated catalyst, by investigating the ignition delay issue increasing the future biofuel mixing ratios.

## METHODS

### Test Engine and Operating Conditions

The test engine utilized in the present study consisted of a four-cylinder direct-injection diesel engine with a turbocharger, an intercooler, and an after-treatment system, which meets Japan's Post New Long Term emission regulations. The after-treatment system was made up of a diesel oxidation catalyst (DOC) and a c-DPF. Table 1 lists detailed specifications of the test engine. DOC catalyzes the oxidation of CO, NO, and hydrocarbons (HC). The engine was operated on an engine dynamometer according to the Japanese JE05 transient cycle for 1830 seconds, implementing three different engine operating conditions: without the after-treatment system (engine-out); with the after-treatment system (tailpipe-out); and during active regeneration with the after-treatment system (regen).

The c-DPF is a wall-flow-type filter coated with precious metal. The c-DPF regeneration starts by determining whether or not the differential pressure between the inlet and the outlet of the c-DPF itself is smaller or greater than a certain value. The burning of the accumulated soot in the c-DPF is possible using the heat supplied by the exhaust gas. Accumulated soot can be burned with the target temperature for c-DPF regeneration set in advance. The temperature of the exhaust gas is made to rise by the DOC-effected oxidation of the fuel injected into the exhaust pipe at the position of the inlet of the DOC. Regeneration started at the beginning of the JE05 test cycle, and it proceeded for about one third of the length of the JE05 test. Before performing the test of the regeneration conditions, c-DPF was treated at high temperature in order to remove all the soot collected within it by electric furnace; subsequently, the JE05 test cycle was repeated eight times. Active regeneration was initiated at the ninth JE05 test cycle. The test engine and particle sampling system are depicted in Fig. 1 for the example case of the regen conditions.

### Test Fuels

In the present study, we used a 10% RME biodiesel blend

**Table 1.** Specification of the test engine.

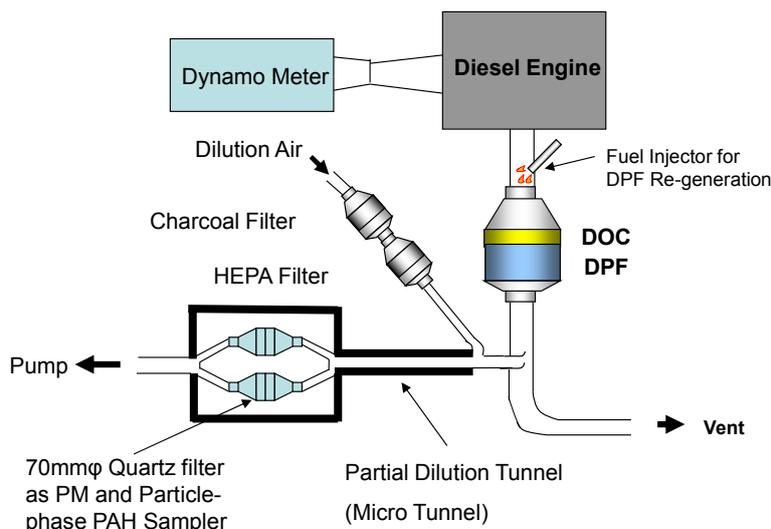| Engine displacement | 2.99 L |
|---|---|
| Cylinder arrangement | Inline, four cylinders, turbocharged |
| Bore × stroke | φ95.4 mm × 104.9 mm |
| Compression ratio | 17.5 |
| Max. power | 110 kW/2800 rpm |
| Max. torque | 375 Nm/1600–2800 rpm |
| After-treatment system | DOC + c-DPF |
| Emission regulation | Japan post new long term |

**Fig. 1.** Test engine and sampling system (c-DPF active regeneration engine operating condition used as an example).

fuel and a D fuel. The main properties of these two fuels are detailed in Table 2. A D fuel is widely used in Japan. A 10% RME biodiesel blend has a higher cetane number, density, and viscosity, and a lower calorific value than D. Notably, the sulfur content is less than 10 ppm for both fuels.

### Particulate Sampling

We used a partial flow dilution system (MDLT-1302 Micro Dilution Tunnel; HORIBA) to dilute and cool the exhaust for particulate sampling; the flow rate of this was set to 80 L min$^{-1}$. The exhaust division ratio of the partial flow dilution tunnel was held constant at 600.

Although diesel exhaust particles are usually collected on a Teflon-coated glass-fiber filter, we had to use quartz-fiber filters instead because we utilized thermal desorption-gas chromatograph-mass spectrometry (TD-GC-MS) for the analysis of PAHs and a carbon analyzer for the analysis of elemental and organic carbon. Before sampling, the quartz fiber filters (Tissuquartz 2500QAT-UP; Pall Corp.) were baked in an electric furnace while being exposed to atmospheric air for 1 h at 350°C. Before and after sampling, the filters were conditioned for 24 h in a chamber characterized by a controlled temperature and relative humidity: 22 ± 3°C and 40 ± 5%, respectively. The filters were then weighed with a microbalance (1-µg readability; M3P-F; Sartorius AG, Goettingen, Germany). At the sampling stage, diesel exhaust particulates were

collected on a 60-mm-diameter area of a 70-mm-diameter filter. After weighing, the filters were stored at –80 ± 2°C until analysis.

### Measurement of the Size Distribution and Number Concentration of the Exhaust Particles

The size distribution and number concentration of the diluted exhaust particle emissions were also measured using the Engine Exhaust Particle Sizer (EEPS) 3090 Spectrometer (TSI Inc., MI, USA). This instrument can measure particles from 5.6 to 560 nm with a high resolution (10 Hz). The dilution ratio was fixed 10 in all of three engine operating conditions. In addition, sampling method was same in at all samplings.

### PAHs Analysis Using Direct-injection Thermal Desorption Gas Chromatography-Mass Spectrometry

The use of direct-injection thermal desorption (TD) gas chromatography-mass spectrometry (GC-MS) for the analysis of organic compounds, such as PAHs, *n*-alkanes, and *n*-monocarboxylic acids, in atmospheric aerosols or automobile exhaust particles has been reported (Neusüss *et al.*, 2000; Waterman *et al.*, 2000; Falkovich and Rudich, 2001; Hays *et al.*, 2003; Ho and Yu, 2004; Hays *et al.*, 2007; Fushimi *et al.*, 2007; Iwakiri *et al.*, 2007; Lavrich and Hays, 2007; Shibata *et al.*, 2010a, b). TD-GC-MS does not require organic solvent extraction and it relies on direct

**Table 2.** Properties of the test fuels.

| Type | 10% RME biodiesel | Petroleum diesel |
|---|---|---|
| Cetane number | 57.5 | 55.6 |
| Density (g cm$^{-3}$) | 0.8498 | 0.8303 |
| Viscosity @ 30°C (mm$^2$ s$^{-1}$) | 4.182 | 3.464 |
| Calorific value (kJ kg$^{-1}$) | 42,760 | 45,850 |
| Sulfur content (mass ppm) | 6 | 7 |
| Distillation @ 30% (°C) | 263.5 | 257.5 |
| Distillation @ 50% (°C) | 288 | 280.5 |
| Distillation @ 80% (°C) | 326 | 317 |

sample injection. An effective way of suppressing the adsorption of samples onto the injection wall would be to cool and concentrate the thermally desorbed PAHs upstream of the GC column, followed by TD again (Iwakiri *et al.*, 2007).

To determine and quantify the presence of PAHs in the particle-phase of diesel exhaust, we used and optimized the conditions for TD-GC-MS combined with a cryogenic-focus trap and selected-ion monitoring (SIM). We also utilized a deuterated, mixed internal standard including all each component of PAH of our target of analysis. This analytical method is more effective to acquire good peak separation and high sensitivity compared to organic solvent-Soxhlet extraction and concentration method.

The PAHs were analyzed using a T-Dex II TD system (GL Sciences Inc., Tokyo, Japan) installed on a Bruker GC-3800GC with a 300-MS (Bruker Corp., MA, USA). The TD tube (89-mm length, 4-mm i.d., 6-mm o.d.; Pyrex) was automatically placed in the TD area under the injection port in the upper part of the GC system. The cryogenic-focus trap system was located below the TD area in the GC oven and was cooled initially at –50°C with liquid nitrogen until reheated. We selected 300°C as the TD temperature because at this temperature, pyrolysis is suppressed and PAHs on the particle make desorption effective. The TD tube was heated from 45°C (for 1 min) to 300°C (for 10 min) at a rate of 5°C $s^{-1}$ by means of a split (1:1)-mode injection. Desorbed compounds were collected in the cryogenic-focus trap at –50°C cooled by liquid nitrogen in a TD tube (0.53 mm i.e., inert fused silica capillary column) and reheated from –50°C (for 1 min) to 300°C (for 10 min) at a rate of 50°C $s^{-1}$ and then were sent to capillary column (30-m length, 0.25-mm i.d., 0.25-μm film thickness; VF-5ms; Agilent Technologies, Inc., Santa Clara, LA, USA) The GC was heated from 60°C (for 3 min) to 200°C at a rate of 15°C $min^{-1}$ and then to 325°C (for 10 min) at a rate of 5°C $min^{-1}$. The helium carrier gas was supplied at 1.3 mL $min^{-1}$. SIM mode was used for quantitative analysis in this study. The GC inlet injector, ion-source, and transfer-line temperatures were 280°C, 230°C, and 280°C, respectively. For quantification of the PAHs, a Standard Reference Material solution, SRM 1647e, including sixteen PAHs was purchased from National Institute of Standards and Technology (NIST; Gaithersburg, MD, USA) and diluted with HPLC-grade acetonitrile to prepare calibration curves. In addition, to increase the accuracy of quantification, we used PAH Cocktail for CARB Method 429 as an internal standard solution including sixteen deuterated all-target PAHs purchased from Cambridge Isotope Laboratories, Inc. (CIL; Andover, MA, USA) and diluted with 2,2,4-trimethylpentane. Before sampling and after each analysis, the TD tubes were cleaned with acetone for 30 min at 50°C in the ultrasonic bath and dried at 80°C in electronic furnace.

A collected particle sample on the quartz filter was punched to be 10 mm in diameter and placed in the middle of an empty TD tube with glass frit. Additionally, we injected diluted internal standard solution on another 10-mm quartz filter and set into the middle on a TD tube above the sample filter. Twelve 3–6-ring PAHs were analyzed within 1 h.

### Elemental and Organic Carbon Analysis Using a Carbon Analyzer

Elemental carbon (EC) and organic carbon (OC) were analyzed with a thermal/optical carbon analyzer, and implementing the IMPROVE protocol (OC1: 120°C, OC2: 250°C, OC3: 450°C, OC4: 550°C (under 100% He atmosphere), EC1: 550°C, EC2: 700°C, EC: 800°C (under 2% $O_2$/98% He atmosphere) (Chow *et al.*, 1993, 2001). Similar to what was done for PAH analysis, an 8-mm hole (with a surface area of 0.503 $cm^2$) was punched in the quartz filter containing the collected particle sample, and the filter thus processed was placed in the stage of the carbon analyzer.

## RESULTS AND DISCUSSION

### Size Distribution and Number Concentration of Particles

Fig. 2 denotes the size distribution and number concentration of the engine exhaust particle emissions using D fuel and 10% RME biodiesel blend under the tailpipe-out engine operating condition. Two peaks of each size distribution were observed using D fuel and 10% RME biodiesel blend. The bimodal peaks were observed at approximately 11 and 70 nm when D fuel was used, whereas they were observed at 11 and 110 nm when 10% RME biodiesel blend was used. The sizes and number concentrations of the smaller peaks were the same for both fuels; however, those of the larger peaks were different. The larger peak was greater and more spread out and the number concentration was higher while using 10% RME biodiesel blend than that observed while using D fuel.

### Regulated Emissions

The amounts of regulated species CO, $CO_2$, THC, and $NO_x$ emitted from the test diesel engine powered with either D fuel or 10% RME fuel are reported in Fig. 3. The test engine was operated under engine-out, tailpipe-out, and regen conditions.

Under the engine-out operating condition, when the engine was powered with 10% RME fuel, the CO emission levels were slightly higher and the THC emission levels slightly lower than when it was powered with D fuel. Under these two engine operating conditions, no significant differences in emission levels were observed. Under the regen engine operating conditions, no significant differences were observed for the emission levels of CO and $NO_x$; however, THC emissions were higher when the engine was powered with 10% RME fuel than when it was powered with D fuel. In addition, $NO_x$ emission levels under the regen engine operating conditions were determined to be approximately twice those measured under the other two engine operating conditions. It was assumed that this difference was because under the regen engine operating conditions, the temperature of the exhaust rises above 550°C.

Some researchers have reported that various types of biodiesel blends can improve the combustion efficiency and reduce emissions of CO, THC, PAHs, and PM with respect to D fuels (Zhang *et al.*, 2011; Tsai *et al.*, 2014). In the case of the low-percentage RME blend fuel that has been
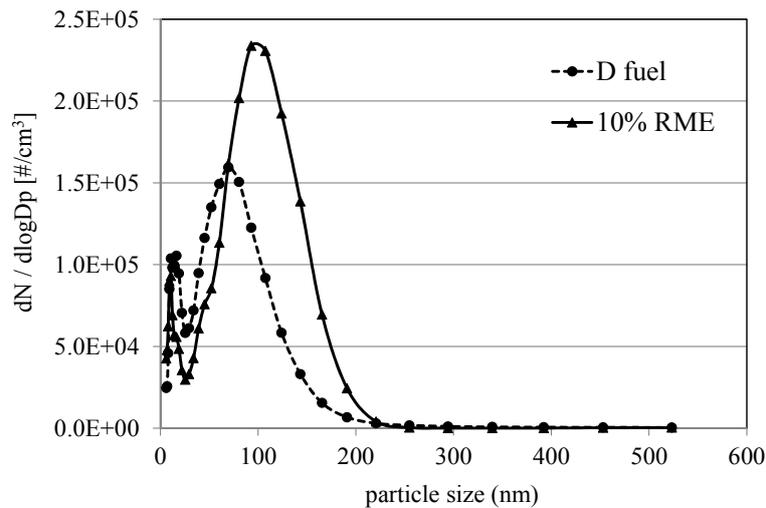
**Fig. 2.** Size distribution and number concentration of the tailpipe-out exhaust particle emissions using petroleum diesel (D) fuel and 10% RME biodiesel blend.
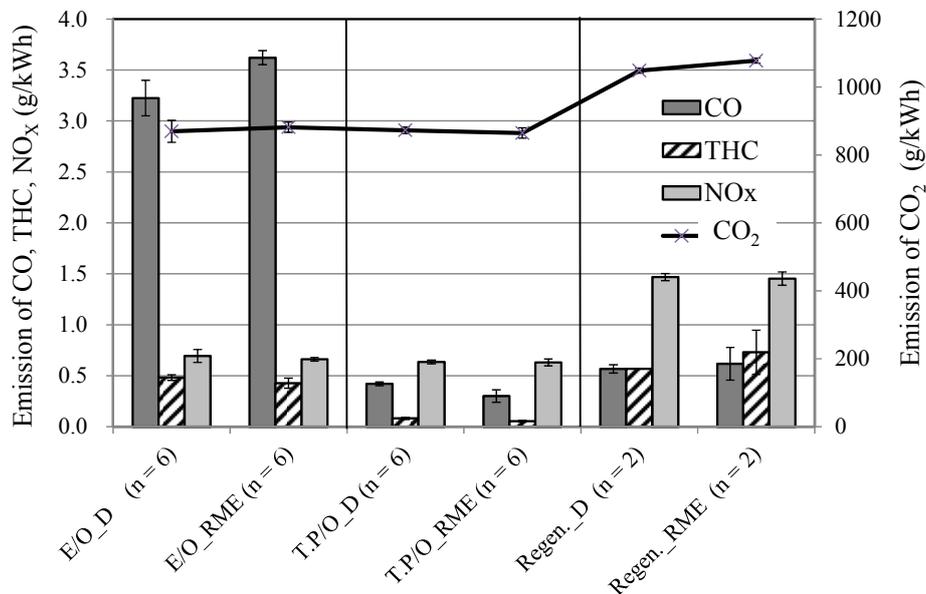


**Fig. 3.** Emissions of CO, $CO_2$, total hydrocarbons (THC), and $NO_x$ associated with the use of petroleum diesel (D) fuel or 10% RME fuel to power a test engine operated under three different conditions: engine-out (E/O), tailpipe-out (TP/O), and regeneration (regen).

utilized in this study, under engine-out and tailpipe-out operating conditions, no significant changes in the level of $NO_x$ emissions were observed with respect to the case of the engine powered with D fuel. By contrast, under the mentioned engine operating conditions, the THC emissions were lower when 10% RME biodiesel blend was used than when D fuel was used, a result consistent with those of the research reports alluded to above. Except for the case of the engine-out operating conditions, the CO emission levels either were lower when 10% RME biodiesel blend was used or displayed no significant difference. It was assumed that these results were because biodiesel blend fuels contain more oxygen than D fuels, so that biodiesel can be more easily oxidized than D, leading to a reduction in the

amount of adsorbed HC and OC. Under the regen engine operating conditions, the emission levels of CO, and THCs were higher than their counterparts measured under the tailpipe-out engine operating conditions.

To regenerate c-DPF and clean it up from adsorbed soot particles, it is necessary to raise the DOC inlet temperature above 250°C so as to trigger catalyst activation. Because the 10% RME biodiesel blend has a 6.7% lower calorific value than D, under the regen engine operating conditions, the amount of 10% RME biodiesel fuel consumed before reaching the target temperature was 5 g $kWh^{-1}$ higher than the corresponding consumed amount of D fuel. Therefore, it was considered that the THC emissions for 10% RME fuel were higher than those for D fuel. The additional fuel

consumption observed under regeneration conditions with respect to the non-regeneration conditions when 10% RME biodiesel blend was used as the fuel was 293 g test$^{-1}$, whereas this parameter was 263 g test$^{-1}$ when D fuel was used instead. We also measured total thermal energy consumption of the combustion associated with the use of the two fuels: The value for this parameter was 12,544 kJ test$^{-1}$ while using the 10% RME biodiesel blend and was 12,048 kJ test$^{-1}$ while using the D fuel. In summary, thermal energy consumption of 10% RME was slightly higher than that released by D fuel. Under the regen engine operating conditions, the evidence thus indicates that the higher THC emissions observed when the 10% RME biodiesel blend was used is the result of a higher fuel consumption level per test. In addition, during the regeneration period of the test mode, the collected particles and the soluble organic fraction (SOF) adsorbed on the particles on the c-DPF are oxidized and are hardly discharged post c-DPF; however,

after the regeneration is completed, the amount of emissions will increase. This effect results from the fact that immediately after regeneration, the particle collection efficiency of c-DPF decreases markedly because particles cannot be collected completely.

### EC and OC emissions

The upper part of Fig. 4 reports the observed emissions of carbonaceous compounds (EC and OC) associated with the use of D fuel and 10% RME biodiesel blend under the three different engine operating conditions. EC2 was the most abundant carbonaceous component in the diesel exhaust particles when the engine-out operating conditions were implemented, and it was also the carbonaceous component for which the largest relative reduction was observed when 10% RME biodiesel blend was used instead of D fuel. By contrast, no significant differences were observed between pairs of the other EC and OC
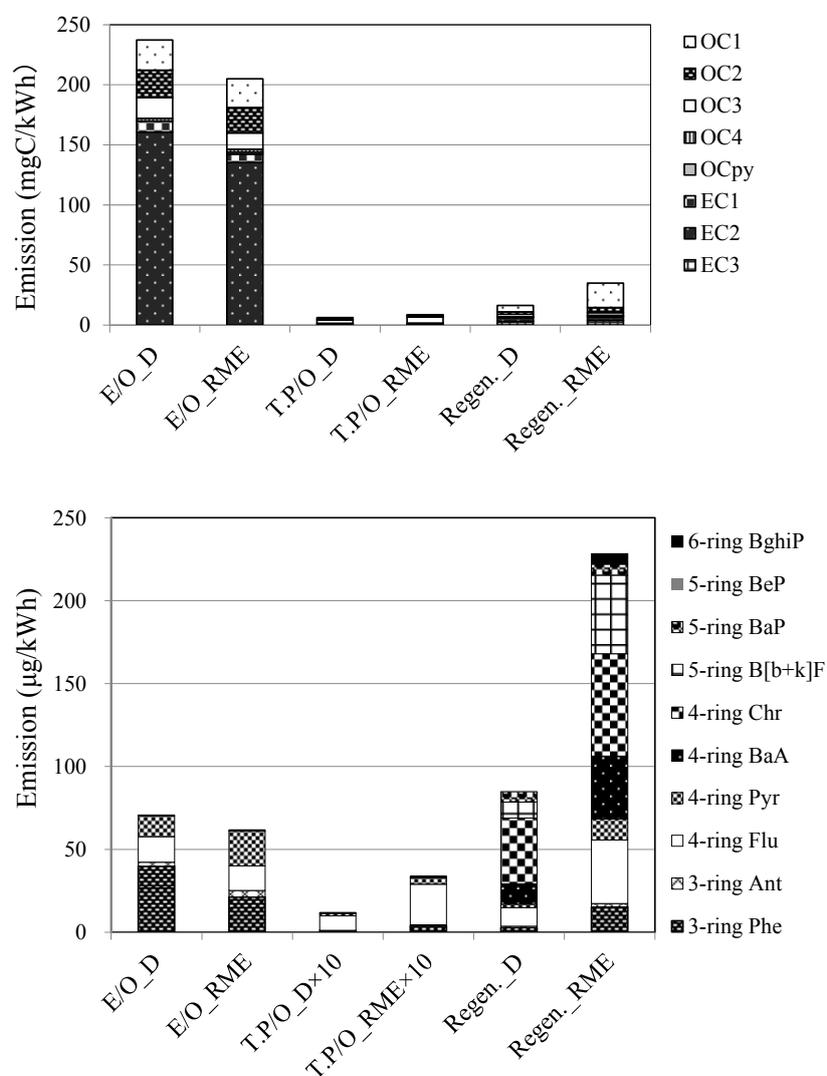


**Fig. 4.** Emissions of carbonaceous compounds, elemental carbon (EC) and organic carbon (OC) (upper graph), and particle-phase emissions of the three- to six-ringed polycyclic aromatic hydrocarbons (lower graph) associated with the use of petroleum diesel (D) fuel or 10% RME biodiesel blend to power a test engine operating under three different conditions: engine-out (E/O), tailpipe-out (TP/O), and regeneration (regen).

components analyzed when 10% RME biodiesel blend was used instead of D fuel to power the test engine operated under the engine-out conditions. Under the tailpipe-out condition, none of the EC or OC components of 10% RME fuel changed significantly when 10% RME biodiesel blend was used instead of D fuel. The reduction in the amounts of EC and OC made possible by the after-treatment system were 99.7% and 91.8%, respectively, when using the D fuel, and 99.5% and 87.8%, respectively, when using the 10% RME biodiesel blend. The evidence therefore indicated that the reduction in OC levels by the after-treatment system was lower when 10% RME was utilized than when the D fuel was utilized. These results are likely to reflect the different properties of the two fuels. Under the regen engine operating conditions, the OC1 and OC2 emissions were higher when using the 10% RME biodiesel blend than when using the D fuel. It was assumed that the OC1 and OC2 contained fuel components that would increase in amount as a result of an increase in fuel consumption. However, because it was not clear whether differences in fuel consumption are the cause of these disparities, the carbonaceous compound emissions per consumed fuel unit calculated.

The upper part of Fig. 5 reports the observed amount for regeneration condition minus non-regeneration conditions for carbonaceous compounds using D fuel and 10% RME fuel. Evidence indicates that the OC1 and OC2 emissions increased significantly from the first scenario to the second; this observation is assumed to result from a decrease in the oxidation capacity of 10% RME biodiesel blend due to its poor calorific value, and low exhaust temperature during the initial regeneration period.

### PAH Emissions

PAHs are distributed between the gas and particle-phase based on their vapor pressure and atmospheric temperature. The two-ringed naphthalene exists almost exclusively in the gas phase, whereas the five- and six-ringed PAHs are predominantly adsorbed on particles. The intermediately sized three- and four-ringed PAHs are distributed between the two phases (Zielinska *et al.*, 2004).

The lower part of Fig. 4 reports data on the particle-phase emissions from the three- to six-ringed PAHs obtained using either 10% RME biodiesel blend or D fuel. In case of the engine-out operating conditions, particle-phase phenanthrene (Phe) emitted when the test engine was powered by 10%
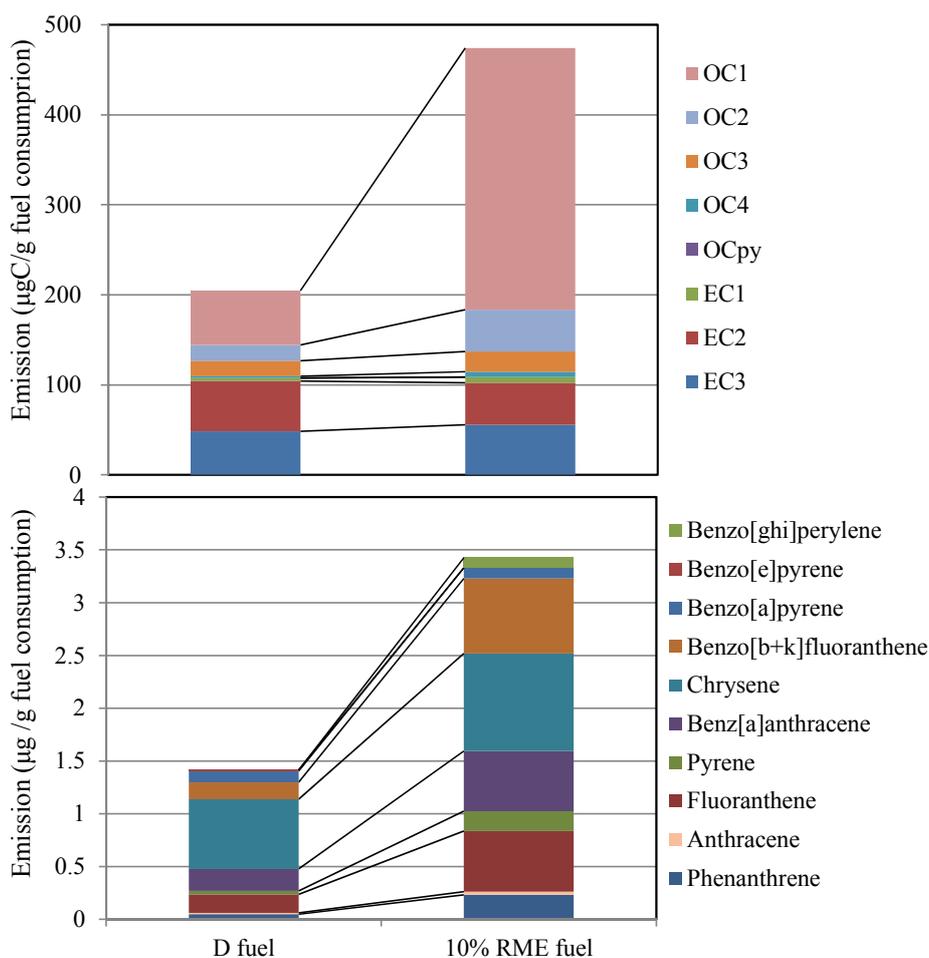


**Fig. 5.** The difference in amount between the regeneration condition and the non-regeneration conditions (the former minus the latter) for carbonaceous compounds (upper graph) and individual polycyclic aromatic hydrocarbons (PAHs) (lower graph) using D fuel and 10% RME fuel.

RME biodiesel blend was half the amount emitted when the engine was powered by D fuel. Conversely, the amount of particle-phase anthracene (Ant) increased slightly when D fuel was replaced with 10% RME biodiesel blend. Overall, when applying the engine-out operating conditions, the total emissions of the three-ringed PAHs were lower when using 10% RME biodiesel blend than when using D fuel. It is considered that the reason is 10% RME fuel contains more oxygen atoms than D fuel. In contrast, these three-ringed PAHs were shown to be scarcely discharged in the particle phase when the tailpipe-out engine operating conditions were used by the oxidation of the catalyst and filter effect. Additionally, the reduction in the amount of Phe and Ant emitted in the particle phase resulting from the installation of the after-treatment system was very high for both fuels: 99.7% and 100.0%, respectively, for D fuel, and 98.2% and 98.3%, respectively, for 10% RME biodiesel blend. Under the regen engine operating conditions, the amount of particle-phase three-ringed PAHs when 10% RME biodiesel blend was utilized were emitted more than when D fuel was utilized. As the calorific value of 10% RME biodiesel blend is 6.7% lower than that of D fuel, it took longer for the c-DPF to reach the target temperature for regeneration (> 550°C) when 10% RME biodiesel blend was utilized than when D fuel was utilized. As the result, the total fuel consumption during JE05-test cycle regeneration was higher when 10% RME biodiesel blend was utilized than when D fuel was utilized. Notably, the total particle-phase emission of the three-ringed PAHs under the regen engine operating conditions were lower than those observed when engine-out operating conditions were implemented.

Under the engine-out operating conditions, the particle-phase four-ringed fluoranthene (Flu) emissions were similar in case of both the fuels but the particle-phase four-ringed pyrene (Pyr) emissions were higher when 10% RME biodiesel blend was used to power the test engine. Under the tailpipe-out engine operating conditions, the particle-phase Flu emissions were also higher when 10% RME fuel was used to power the test engine. This evidence suggests, therefore, that the use of 10% RME fuel results in incomplete combustion caused by its poor evaporation and it is believed the ratio of SOF/soot is higher compared with D fuel. The reductions in particle-phase Flu and Pyr emissions achieved by the after-treatment system were 94.3% and 99.1% when D fuel was utilized, and 83.5% and 98.2%, respectively, when 10% RME biodiesel blend was utilized. Therefore, when using 10% RME biodiesel blend, the reductions in particle-phase Flu and Pyr emissions resulting from the use of the after-treatment system are lower than their counterparts observed for three-ringed PAHs. The particle-phase emissions of the other two four-ringed PAHs investigated (BaA and Chr) are too low for their reductions associated with the use of the after-treatment system to be evaluated. Notably, under the regen engine operating conditions, the particle-phase emissions of all four four-ringed PAHs targeted for analysis in this study increased significantly when 10% RME biodiesel blend was utilized to power the test engine instead of D

fuel. Furthermore, the period of regeneration observed to be necessary when using 10% biodiesel blend was longer than its counterpart observed when using D fuel. The difference caused fuel consumption and the particle-phase emissions of some PAHs to increase when 10% RME biodiesel blend was used instead of D fuel.

Under the engine-out and tailpipe-out engine operating conditions, none of the five- and six-ringed PAHs benzo($b+k$) fluoranthene (B($b+k$)F), benzo($a$)pyrene (BaP), and benzo($g,h,i$)perylene (BghiP) was actually detected; however, under the regen engine operating conditions, the B($b+k$)F and BghiP emissions increased when 10% RME biodiesel blend was utilized to power the test engine instead of D fuel. The particle-phase emissions of some of the three-, four-, and five-ringed PAHs in the case of 10% RME fuel also increased on the regeneration condition because the filter collection efficiency decreases immediately after the regeneration period, and the particles slip through c-DPF.

The lower part of Fig. 5 reports the observed regeneration amount minus the non-regeneration amount for selected PAHs while using D fuel and 10% RME fuel. The emissions of eight PAHs contained in SOF increased in the incomplete combustion of 10% RME biodiesel blend.

## CONCLUSIONS

The emissions of both regulated and unregulated species, viz., CO, $CO_2$, THC, $NO_x$, EC, OC, and PAHs, from a modern diesel engine equipped with an after-treatment system (consisting of a diesel oxidation catalyst and a c-DPF) and powered by either a 10% RME biodiesel blend or petroleum diesel fuel were quantified for three different states: when the after-treatment system was deployed (engine-out), when the after-treatment system was not deployed (tailpipe-out), and when the after-treatment system was deployed and the c-DPF was regenerating (regen). Although switching between the states while using the biodiesel blend showed no significant effects on the regulated emissions of CO, $CO_2$, THC, and $NO_x$, some differences were detected in the unregulated emissions of EC, OC, and PAHs.

The analysis results of the carbonaceous components indicated that during engine-out, the EC2 emissions were slightly lower while using the 10% RME biodiesel blend than the diesel fuel. Notably, EC2 was also the most abundant EC component identified in the diesel exhaust. However, the OC1 and OC2 emissions increased during regen while using the biodiesel blend because of large fuel consumption. The filter collection efficiency also decreased in the period immediately following regeneration, allowing particles to slip through the c-DPF; in particular, we observed more three-, four-, and five-ringed PAHs. Despite this increase, the amount of PAHs emitted by the engine was very small compared to that of carbonaceous components (EC and OC) while using the biodiesel blend. The c-DPF also required a longer regeneration period with the blend than with the petroleum diesel fuel.

Substituting diesel fuel with this biodiesel blend reduces the emission of EC2 for engines without an after-treatment system without significantly increasing the emission of

EC, OC, and PAHs for engines with an after-treatment system. Although, as aforementioned, the emissions of OC1, OC2, and some PAHs actually increased during the regeneration phase with the biodiesel blend, presumably as a result of its decreased oxidation capacity at low exhaust temperatures due to its lower calorific value, these issues can be resolved by improving the control technology for c-DPFs and reducing the frequency of regeneration.

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## SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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