

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

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## Abstract

In this study, the impact of using 10% rapeseed methyl ester (RME) blended biodiesel fuel on the identity and quantity of the chemicals emitted by a modern diesel engine was investigated. The diesel engine that was utilized met Japan's Post New Long Term emission regulations and was equipped with an after-treatment system comprising a diesel oxidation catalyst and a catalyzed diesel particulate filter (c-DPF). Exhaust gas sampling was conducted with three engine operating conditions, which were engine-out, tailpipe-out, and regeneration of the after-treatment system during the Japanese JE05 test cycles. Evidence from this study indicated that the use of 10% RME biodiesel had no significant impact on the regulated emissions of CO, CO<sub>2</sub> total hydrocarbons, and NO<sub>x</sub>, regardless of the sampling conditions. However, some effects were evident on the emissions of elemental carbon, organic carbon, and polycyclic aromatic hydrocarbons (PAHs), which are unregulated. Under the engine-out and tailpipe-out conditions, emissions of the elemental carbon species EC2 associated with the use of 10% RME biodiesel were slightly lower than those associated with the use of petroleum diesel (D) fuel; however, an increase in the organic carbon species OC1, OC2, and some PAHs was observed under regeneration conditions because of the sizable consumption of 10% RME biodiesel compared to D fuel. These results from our study confirmed that 10% RME blended biodiesel is a promising alternative to fossil fuels for diesel engines, but it is important to grasp the behavior of such detailed components and counter the impact of increase in mixing ratios.

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

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## 36 INTRODUCTION

37

38 Biodiesel is regarded as an alternative to fossil fuels for powering compression ignition (CI)  
39 engines because this type of fuel is renewable, carbon-neutral, and biodegradable. Biodiesel is  
40 almost entirely made from edible vegetable oils (e.g., soybean, palm, sunflower oils), and plant  
41 seed oils (e.g., rapeseed and linseed oils). Research focusing on biodiesel and aimed at addressing  
42 the air pollution and global warming resulting from the use of fossil fuels is actively being  
43 pursued around the world. Additional characteristics that render biodiesel appealing from a  
44 research and environmental standpoint are that it has a narrower boiling range than petroleum  
45 diesel (D) fuel, as well as a higher viscosity and cetane number, in conjunction with a lower  
46 volatility (Zheng *et al.*, 2006; He *et al.*, 2016). Reports published over the past few years indicate  
47 that the volume-based ranking of vegetable oil is as follows: soybean oil is the most widely  
48 produced vegetable oil, followed by palm oil and then rapeseed. Because of higher productivity  
49 per area and lower production cost, palm oil is one of the most appealing raw materials for  
50 biodiesel production. Soybean oil methyl ester is currently commercially available in the United  
51 States, whereas rapeseed methyl ester (RME) is available in some European countries (Kinoshita  
52 *et al.*, 2006). In Europe, biodiesel is mostly manufactured to meet the requirements (He *et al.*,  
53 2016).

54 Given that, in general, at a molecular level biodiesel contains more oxygen atoms than D fuel,  
55 biodiesel-associated NO<sub>x</sub> emissions can also be higher than D fuel's emissions (Babu *et al.*, 2003;

56 Sze *et al.*, 2007; Robbins *et al.*, 2011). Zhong *et al.* found that the ignition delay decreased with  
57 the increasing blending ratio of second-generation biodiesel (SGB), such as non-edible feedstocks,  
58 waste or recycle oils, and animal fats, as cetane number is an important factor for affecting the  
59 ignition delay. They concluded that when SGB blends in fuel, it reduces NO<sub>x</sub>; however, the use of  
60 SGB can weaken the trade-off relation between particulate matter (PM) and NO<sub>x</sub>. This is thought  
61 to be an advantage to solve the problems related to first-generation biodiesel.

62 Most of the studies concentrating on emissions originating from CI engines powered by  
63 biodiesel focused on regulated pollutants, such as particulate matter (PM), total hydrocarbons  
64 (THC), NO<sub>x</sub>, and CO (Zhang *et al.*, 2011). The size of PM is also an important factor for  
65 affecting human health. Peters *et al.* conducted a short-term research on epidemiology. Their  
66 results indicated that size distribution of ambient particles helps to elucidate the properties of  
67 ambient aerosols responsible for the effects on human health. Chien *et al.* measured the size  
68 distribution of PM and PAHs. Furthermore, they indicated that for most biodiesel blending  
69 mixtures in four size ranges, the percentages of PAH emission reduction were higher than those  
70 of PM emission. Ajtai *et al.* reported that the ratio of biodiesel to petroleum diesel in the total fuel  
71 blend can influence both the total number and volume concentration and distribution of the  
72 particle emission. The total number and volume concentration emitted by the diesel engine  
73 decreased with increasing revolution of engine per minute and rated torque of engine in case of

74 all fuel blend types. Their observations revealed that the extent of the biodiesel content in the  
75 total fuel amount can influence the total volume and number of emitted particulates.

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

85 This present study concentrates on evaluating the emissions of carbonaceous components and  
86 particle-phase polycyclic aromatic hydrocarbons (PAHs) with a diesel engine powered by either a  
87 10% RME biodiesel blend or a D fuel. In particular, three engine operating conditions were  
88 utilized in our research: engine-out as without the after-treatment system condition, tailpipe-out  
89 as with the after-treatment system condition, and during active regeneration of catalyzed diesel  
90 particulate filter (c-DPF) condition under the Japanese JE05 transient test cycle. This research is  
91 useful for finding the best countermeasure such as adding heat generation improver, for example

92 electrically heated catalyst by investigating some issues presented toward increasing the future  
93 biofuel mixing ratios.

94

## 95 **METHODS**

96

### 97 *Test engine and operating conditions*

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

107 The c-DPF is a wall-flow-type filter coated with precious metal. The c-DPF regeneration starts  
108 by determining whether or not the differential pressure between the inlet and the outlet of the c-  
109 DPF itself is smaller or greater than a certain value. The burning of the accumulated soot in the c-  
110 DPF is possible using the heat supplied by the exhaust gas. Accumulated soot can be burned with  
111 the target temperature for c-DPF regeneration of set in advance. The temperature of the exhaust

112 gas is made to rise by the DOC-effected oxidation of the fuel injected into the exhaust pipe at the  
113 position of the inlet of the DOC. Regeneration started at the beginning of the JE05 test cycle, and  
114 it proceeded for about one third of the length of the JE05 test. Before performing the test of the  
115 regeneration conditions, c-DPF was treated at high temperature in order to remove all the soot  
116 collected within it by electric furnace ; subsequently, the JE05 test cycle was repeated eight times.  
117 Active regeneration was initiated at the ninth JE05 test cycle. The test engine and particle  
118 sampling system are depicted in Fig. 1 for the example case of the Regen conditions.

#### 120 ***Test fuels***

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

#### 126 ***Particulate sampling***

127 We used a partial flow dilution system (HORIBA micro tunnel model: MDLT1302) to dilute  
128 and cool the exhaust for particulate sampling; the flow rate of this was set to 80 Lmin<sup>-1</sup>. The  
129 exhaust division ratio of the partial flow dilution tunnel was held constant at 600.

130 Although diesel exhaust particles are usually collected on a Teflon-coated glass-fiber filter, we  
131 had to use quartz-fiber filters instead because we utilized thermal desorption–gas  
132 chromatography–mass spectrometry for the analysis of PAHs and a carbon analyzer for the  
133 analysis of elemental and organic carbon. Before sampling, the quartz-fiber filters (Tissuquartz  
134 filter 2500QAT-UP, Pall Corporation) were baked in an electric furnace while being exposed to  
135 atmospheric air for 1 h at 350°C. Before and after sampling, the filters were conditioned for 24 h  
136 in a chamber characterized by a controlled temperature and relative humidity:  $22 \pm 3^\circ\text{C}$  and  $40 \pm$   
137  $5\%$ , respectively. The filters were then weighed with a microbalance (readability  $1 \mu\text{g}$ , M3P-F,  
138 Sartorius AG, Goettingen, Germany). At the sampling stage, diesel exhaust particulates were  
139 collected on a 60-mm-diameter area of a 70-mm-diameter filter. After weighing, the filters were  
140 stored at  $-80 \pm 2^\circ\text{C}$  until analysis.

141

#### 142 ***Measurement of the size distribution and number concentration of the exhaust particles***

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

148

149 *PAHs analysis using thermal desorption-direct-injection gas chromatography-mass*  
150 *spectrometry*

151 The use of thermal desorption (TD)–direct-injection gas chromatography–mass spectrometry  
152 (GC–MS) for the analysis of organic compounds, such as PAHs, *n*-alkanes, and *n*-  
153 monocarboxylic acids, in atmospheric aerosols or automobile exhaust particles has been reported  
154 (Neusüss *et al.*, 2000; Waterman *et al.*, 2000; Falkovich and Rudich, 2001; Hays *et al.*, 2003,  
155 2007; Ho and Yu, 2004; Fushimi *et al.*, 2007; Iwakiri *et al.*, 2007; Lavrich and Hays, 2007;  
156 Shibata *et al.*, 2010a, b). TD–GC–MS does not require organic solvent extraction and it relies on  
157 direct sample injection. An effective way of suppressing the adsorption of samples onto the  
158 injection wall would be to cool and concentrate the thermally desorbed PAHs upstream of the GC  
159 column, followed by TD again (Iwakiri *et al.*, 2007).

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



165 The PAHs were analyzed using a T-Dex II TD system (GL Sciences Inc, Tokyo, Japan)  
166 installed on a Bruker GC-3800 GC with a 300-MS (Bruker Corporation, MA, USA). The TD  
167 tube (Pyrex, 89 mm length, 4 mm i.e., 6 mm o.d.) was automatically placed in the TD area under  
168 the injection port in the upper of GC system. The cryogenic-focus trap system was located below  
169 the TD area in the GC oven and was cooled initially at  $-50^{\circ}\text{C}$  with liquid nitrogen until reheated.  
170 We selected  $300^{\circ}\text{C}$  as the TD temperature because at this temperature, pyrolysis is suppressed  
171 and PAHs on the particle make desorption effective. The TD tube was heated from  $45^{\circ}\text{C}$  (for 1  
172 min) to  $300^{\circ}\text{C}$  (for 10 min) at a rate of  $5^{\circ}\text{C s}^{-1}$  by means of a split (1:1)-mode injection. Desorbed  
173 compounds were collected in the cryogenic-focus trap at  $-50^{\circ}\text{C}$  cooled by liquid nitrogen in a TD  
174 tube (0.53 mm i.e., inert fused silica capillary column) and reheated from  $-50^{\circ}\text{C}$  (for 1 min) to  
175  $300^{\circ}\text{C}$  (for 10 min) at a rate of  $50^{\circ}\text{C s}^{-1}$  and then were sent to capillary column (Model VF-5ms;  
176  $30\text{ m} \times 0.25\text{ mm}$  i.e.,  $0.25\text{ }\mu\text{m}$  i.e., film thickness, Agilent Technologies Inc.; Santa Clara, LA,  
177 USA) The GC was heated from  $60^{\circ}\text{C}$  (for 3 min) to  $200^{\circ}\text{C}$  at a rate of  $15^{\circ}\text{C}/\text{min}$  and then to  
178  $325^{\circ}\text{C}$  (for 10 min) at a rate of  $5^{\circ}\text{C min}^{-1}$ . The helium carrier gas was supplied at  $1.3\text{ mL min}^{-1}$ .  
179 SIM mode was used for quantitative analysis in this study. The GC inlet injector, ion-source, and  
180 transfer-line temperatures were  $280^{\circ}\text{C}$ ,  $230^{\circ}\text{C}$ , and  $280^{\circ}\text{C}$ , respectively. For quantification of the  
181 PAHs, a standard reference material SRM 1647e solution including sixteen PAHs was purchased  
182 from National Institute of Standards and Technology (NIST; Gaithersburg, MD, USA) and

183 diluted with HPLC-grade acetonitrile to prepare calibration curves. In addition, to increase the  
184 accuracy of quantification, we used PAH Cocktail for CARB Method 429 as an internal standard  
185 solution including sixteen deuterated all-target PAHs purchased from Cambridge Isotope  
186 Laboratories, Inc. (CIL; Andover, MA, USA) and diluted with 2,2,4-trimethylpentane. Before  
187 sampling and after each analysis, the TD tubes were cleaned with acetone for 30 minutes at 50°C  
188 in the ultrasonic bath and dried at 80°C in electronic furnace.

189 Collected particle sample on the quartz filter was punched 10 mm diameter, and placed in the  
190 middle of an empty TD tube with glass frit. Additionally, we injected diluted internal standard  
191 solution on another 10 mm quartz filter and set into the middle on a TD tube above the sample  
192 filter. Twelve PAHs (3- to 6- ring PAHs) were analyzed within 1 hour.

193

#### 194 ***Elemental and organic carbon analysis using a carbon analyzer***

195 Elemental carbon (EC) and organic carbon (OC) were utilized a Thermal/Optical carbon  
196 analyzer, and implementing the IMPROVE method (Chow *et al.*, 1993, 2001). Similar to what  
197 was done for PAH analysis, an 8-mm hole (with a surface area of 0.503 cm<sup>2</sup>) was punched in the  
198 quartz filter containing the collected particle sample, and the filter thus processed was placed in  
199 the stage of the carbon analyzer. The analyzer was then heated to 120°C (OC1; organic carbon  
200 which volatilizes from the sample filter between room temperature and 120°C under 100%

201 helium atmosphere), 240 °C (OC2; between 120°C and 240 °C), 450 °C (OC3; between 240 °C  
202 and 450 °C), and 550 °C (OC4; between 450°C and 550 °C) in a 100% helium atmosphere and to  
203 550 °C (EC1; elemental carbon which volatilized from the sample filter at 550 °C under 2%  
204 oxygen, 98% helium atmosphere), 700 °C (EC2; between 550°C and 700 °C) and 800 °C (EC3;  
205 between 700°C and 800 °C) in an oxidizing atmosphere (2% oxygen, 98% helium).

206

## 207 **RESULTS AND DISCUSSION**

208

### 209 *Size distribution and number concentration of particles*

210 Fig. 2 denotes the size distribution and number concentration of the engine exhaust particle  
211 emissions using D fuel and 10% RME biodiesel blend under the tailpipe-out engine operation  
212 condition. Two peaks of each size distribution were observed using D fuel and 10% RME  
213 biodiesel blend. The bimodal peaks were observed at approximately 11 and 70 nm when D fuel  
214 was used, whereas they were observed at 11 and 110 nm when 10% RME biodiesel blend was  
215 used. The size of the smaller peaks is same in case of both the fuels; however, the size and  
216 number concentration of the smaller peaks were same and those of larger peaks were different in  
217 case of both the fuels. The larger peak was greater and more spread and the number concentration  
218 was higher while using 10% RME biodiesel blend than that observed while using D fuel.

219

### 220 *Regulated emissions*

221 The amounts of regulated species CO, CO<sub>2</sub>, THC, and NO<sub>x</sub> emitted from the test diesel engine  
222 powered with either D fuel or 10% RME fuel are reported in Fig. 3. The test engine was operated  
223 under engine-out, tailpipe-out, and Regen conditions.

224 Under the engine-out operating condition, when the engine was powered with 10% RME fuel,  
225 the CO emission levels were slightly higher and the THC emission levels slightly lower than  
226 when it was powered with D fuel. Under these two engine operating conditions, no significant  
227 differences emission levels were observed. Under the Regen engine operating conditions, no  
228 significant differences were observed for the emission levels of CO and NO<sub>x</sub>; however, THC  
229 emission were higher when the engine was powered with 10% RME fuel than when it was  
230 powered with D fuel. In addition, NO<sub>x</sub> emission levels under the Regen engine operating  
231 conditions were determined to be approximately twice those measured under the other two engine  
232 operating conditions. It was assumed that this difference was because, under the Regen engine  
233 operating conditions, the temperature of the exhaust rises above 550°C.

234 Some researchers have reported that various types of biodiesel blends can improve the  
235 combustion efficiency and reduce emissions of CO, THC, PAHs, and PM with respect to D fuels  
236 (Zhang *et al.*, 2011; Tsai *et al.*, 2014). In the case of the low-percentage RME blend fuel that has  
237 been utilized in this study, under engine-out and tailpipe-out operating conditions, no significant  
238 changes in the level of NO<sub>x</sub> emissions were observed with respect to the case of the engine  
239 powered with D fuel. On the contrary, under the mentioned engine operating conditions, the THC  
240 emissions were lower when 10% RME biodiesel blend was used than when D fuel was used, a  
241 result consistent with those of the research reports alluded to above. Except for the case of the  
242 engine-out operating conditions, the CO emission levels either were lower when 10% RME  
243 biodiesel blend was used or displayed no significant difference. It was assumed that these results  
244 were because biodiesel blend fuels contain more oxygen than D fuels, so that biodiesel can be

245 more easily oxidized than D, leading to a reduction in the amount of adsorbed HC and OC. Under  
246 the Regen engine operating conditions, the emission levels of CO, and THCs were higher than  
247 their counterparts measured under the tail-pipe out engine operating conditions.

248 To regenerate c-DPF and clean it up from adsorbed soot particles, it is necessary to raise the  
249 DOC inlet temperature above 250°C, so as to catalyst activation. Because the 10% RME  
250 biodiesel blend has a 6.7% lower calorific value than D, under the Regen engine operating  
251 conditions, the amount of 10% RME biodiesel fuel consumed before reaching the target  
252 temperature was 5 g kWh<sup>-1</sup> higher than the corresponding consumed amount of D fuel, the  
253 amount of D fuel. Therefore, it was considered that the THC emissions for 10% RME fuel were  
254 higher than those for D fuel. The additional fuel consumption observed under regeneration  
255 conditions with respect to the non-regeneration conditions when 10% RME biodiesel blend was  
256 used as the fuel was 293 g test<sup>-1</sup>, whereas this parameter was 263 g test<sup>-1</sup> when D fuel was used  
257 instead. We also measured the total heat of combustion associated with the use of the two fuels:  
258 the value for this parameter was 12,544 kJ test<sup>-1</sup> while using the 10% RME biodiesel blend and  
259 was 12,048 kJ test<sup>-1</sup> while using the D fuel. In summary, although the calorific value of 10%  
260 RME according to the test conditions was slightly higher than that released by D fuel. Under the  
261 Regen engine operating conditions, the evidence thus indicates that the higher THC emissions  
262 observed when the 10% RME biodiesel blend was used is the result of a higher fuel consumption  
263 level per test. In addition, during the regeneration period of the test mode, the collected particles  
264 and the soluble organic fraction (SOF) adsorbed on the particles on the c-DPF are oxidized and  
265 are hardly discharged post c-DPF; however, after the regeneration is completed, the amount of  
266 emissions will increase. This effect results from the fact that immediately after regeneration, the  
267 particle collection efficiency of c-DPF decreases markedly because of particles cannot be  
268 collected completely.

269

270 ***EC and OC emissions***

271 The upper part of Fig. 4 reports the observed emissions of carbonaceous compounds (EC and  
272 OC) associated with the use of D fuel and 10% RME biodiesel blend under the three different  
273 engine operating conditions. EC2 was the most abundant carbonaceous component in the diesel  
274 exhaust particles when the engine-out operating were implemented, and it was also the  
275 carbonaceous which the largest relative reduction was observed when 10% RME biodiesel blend  
276 was used instead of D fuel. On the contrary, no significant differences were observed between  
277 pairs of the other EC and OC components analyzed when 10% RME biodiesel blend was used  
278 instead of D fuel to power the test engine operated under the engine-out conditions. Under the  
279 tailpipe-out condition, none of the EC or OC components of 10% RME fuel changed significantly  
280 when 10% RME biodiesel blend was used instead of D fuel. The reduction in the amounts of EC  
281 and OC made possible by the after-treatment system were 99.7% and 91.8%, respectively, when  
282 using the D fuel, and 99.5% and 87.8%, respectively, when using the 10% RME biodiesel blend.  
283 The evidence therefore indicated that the reduction in OC levels by the after-treatment system  
284 was lower when 10% RME was utilized than when the D fuel was utilized. These results are  
285 likely to reflect the different properties of the two fuels. Under the Regen engine operating  
286 conditions, the OC1 and OC2 emissions were higher when using the 10% RME biodiesel blend  
287 than when using the D fuel. It was assumed that the OC1 and OC2 contained fuel components  
288 that would increase in amount as a result of an increase in fuel consumption. However, because it  
289 is not clear whether differences in fuel consumption are the cause of these disparities, the  
290 carbonaceous compound emissions per consumed fuel unit calculated.

291 The upper part of Fig. 5 reports the observed the amount for regeneration condition minus non-  
292 regeneration conditions for carbonaceous compounds under using D fuel and 10% RME fuel..

293 Evidence indicates that the OC1 and OC2 emissions increased significantly from the first  
294 “scenario” to the second; this observation is assumed to result from a decrease in the oxidation  
295 capacity of 10% RME biodiesel blend due to its poor calorific value, and low exhaust  
296 temperature during the initial regeneration period.

297

### 298 ***PAH emissions***

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

304 The lower part of Fig. 4 reports data on the particle-phase emissions from the three- to six-  
305 ringed PAHs obtained using either 10% RME biodiesel blend or D fuel. In case of the engine-out  
306 operating conditions, particle-phase-phenanthrene (*Phe*) emitted when the test engine was  
307 powered by 10% RME biodiesel blend was half the amount emitted when the engine was  
308 powered by D fuel. Conversely, the amount of particle-phase-anthracene (*Ant*) increased slightly  
309 when D fuel was replaced with 10% RME biodiesel blend. Overall, when applying the engine-out  
310 operating conditions, the total emissions of the three-ringed PAHs were lower when using 10%  
311 RME biodiesel blend than when using D fuel. It is considered that their reason is 10% RME fuel

312 contains more oxygen atoms than D fuel. In contrast, these three-ringed -PAHs were shown to be  
313 scarcely discharged in the particle phase when the tailpipe-out engine operating conditions were  
314 used by the oxidation of the catalyst and filter effect. Additionally, the reduction in the amount of  
315 *Phe* and *Ant* emitted in the particle phase resulting from the installation of the after-treatment  
316 system was very high for both fuels; 99.7% and 100.0% respectively, for D fuel, and 98.2% and  
317 98.3% respectively, for 10% RME biodiesel blend. When the Regen engine operating conditions  
318 were used, the test engine emitted larger amounts of particle-phase three-ringed PAHs were 10%  
319 RME biodiesel blend was utilized than when D fuel was utilized. As the calorific value of 10%  
320 RME biodiesel blend is 6.7% lower than that of D fuel, it took longer for the c-DPF to reach the  
321 target temperature for regeneration (>550°C) when 10% RME biodiesel blend was utilized than  
322 when D fuel was utilized. As the result, the total fuel consumption during JE05-test cycle  
323 regeneration was higher when 10% RME biodiesel blend was utilized than when D fuel was  
324 utilized. Notably, the total particle-phase emission of the three ringed PAHs under the Regen  
325 engine operating conditions were lower than those observed when engine-out operating  
326 conditions were implemented.

327 Under the engine-out operating conditions, the particle-phase-four-ringed fluoranthene (*Flu*)  
328 emissions were similar in case of both the fuels but the particle-phase-four-ringed pyrene (*Pyr*)  
329 emissions were higher when 10% RME biodiesel blend was used to power the test engine. Under



330 the tailpipe-out engine operating conditions, the particle-phase Flu emissions were also higher  
331 when 10% RME fuel was used to power the test engine. This evidence suggests, therefore, that  
332 the use of 10% RME fuel results in incomplete combustion caused by its poor evaporation and it  
333 is believed the ratio of SOF/Soot is higher compared with D fuel. The reductions in particle-phase  
334 -Flu and -Pyr emissions achieved by the after-treatment system were 94.3% and 99.1% when D  
335 fuel was utilized, and, 83.5% and 98.2%, respectively, when 10% RME biodiesel blend was  
336 utilized. Therefore, when using 10% RME biodiesel blend, the reductions in particle-phase -Flu  
337 and -Pyr emissions resulting from the use of the after-treatment system are lower than their  
338 counterparts observed for three-ringed PAHs. The particle-phase emissions of the other two four-  
339 ringed PAHs investigated (-BaA and -Chr) are too low for their reductions associated with the use  
340 of the after-treatment system to be evaluated. Notably, under the Regen engine operating  
341 conditions, the particle-phase emissions of all four four-ringed PAHs targeted for analysis in this  
342 study increased significantly when 10% RME biodiesel blend was utilized to power the test  
343 engine instead of D fuel. Furthermore, the period of regeneration observed to be necessary when  
344 using 10% biodiesel blend was longer than its counterpart observed when using D fuel. The  
345 difference caused fuel consumption and the particle-phase emissions of some PAHs to increase  
346 when 10% RME biodiesel blend was used instead of D fuel.

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

355 The lower part of Fig. 5 reports the observed the regeneration amount minus the non-  
356 regeneration amount for selected PAHs while using D fuel and 10% RME fuel. The emissions of  
357 eight-PAHs increased in the incomplete combustion of 10% RME biodiesel blend and PAHs,  
358 which are components of SOF increased.

359

## 360 **CONCLUSIONS**

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362 The emissions of the regulated and unregulated species of CO, CO<sub>2</sub>, THC, NO<sub>x</sub>, EC, OC, and  
363 PAHs from a modern diesel engine equipped with after-treatment systems and powered by either  
364 10% RME blended biodiesel blend or petroleum diesel fuel were quantified under three different  
365 engine operating conditions: engine-out, tailpipe-out, and DPF active regeneration.

366 The evidence indicated that switching between the three engine operating conditions had no  
367 significant effect on the regulated emissions of CO, CO<sub>2</sub>, THC, and NO<sub>x</sub> while using the 10%  
368 RME biodiesel blend as fuel. However, some effects were detected on the unregulated emissions  
369 of EC, OC, and PAHs.

370 The analysis results of carbonaceous components indicated that when using 10% RME  
371 biodiesel blend, EC<sub>2</sub> emissions were slightly lower than those under the engine-out condition.  
372 Notably, EC<sub>2</sub> was the most abundant EC component identified in the diesel particles. The  
373 emissions of OC<sub>1</sub> and OC<sub>2</sub> measured for the test engine powered by the 10% RME biodiesel  
374 blend increased because of the large fuel consumption under the regeneration conditions. The  
375 filter collection efficiency possibly drops in the initial early period after regeneration and the  
376 particles slip through the DPF during this time; in particular, the emissions of some three-, four-,  
377 and five-ringed PAHs increased because of regeneration when 10% RME biodiesel blend was  
378 used. However, the amount of emitted PAHs was determined to be very small when compared  
379 with that of the carbonaceous components (EC and OC). A longer period of regeneration was  
380 required while using the 10% RME biodiesel blend than that required when it was powered with  
381 petroleum diesel fuel.

382 The results of this study confirmed that 10% RME blended biodiesel is promising alternative to  
383 fossil fuels for diesel engines. Evidence indicates that the use of this alternative fuel can reduce

384 EC2 emissions in an engine where the after-treatment system is not in use; additionally, EC, OC,  
385 and PAH emissions did not significantly increase in an engine powered by 10% RME biodiesel  
386 blend equipped with an after-treatment system that is in use. The emissions of OC1, OC2, and  
387 some PAHs actually increased when the 10% RME biodiesel blend and the c-DPF were used  
388 under regeneration conditions; this phenomenon occurred because the use of the 10% RME  
389 biodiesel blend is associated with more sizable fuel consumption when compared with that using  
390 D fuel, which presumably resulted from the decrease in oxidation capacity at a low exhaust  
391 temperature during the initial of regeneration period because of calorific value of the biodiesel  
392 blend fuel. However, it is expected that these issues will be solved by improving the c-DPF  
393 regeneration control technology for reducing the regeneration frequency.

394

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396

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401

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481 **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

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

Type	10% RME biodiesel	Petroleum diesel
Cetane number	57.5	55.6
Density (g cm <sup>-3</sup> )	0.8498	0.8303
Viscosity @ 30 °C (mm <sup>2</sup> s <sup>-1</sup> )	4.182	3.464
Calorific value (kJ kg <sup>-1</sup> )	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

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511 **Figure Captions**

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

514 **Fig. 2.** Size distribution and number concentration of the tailpipe-out exhaust particle emissions  
515 using petroleum diesel (D) fuel and 10% RME biodiesel blend.

516 **Fig. 3.** Emissions of CO, CO<sub>2</sub>, total hydrocarbon (THC), and NO<sub>x</sub> associated with the use of  
517 petroleum diesel (D) fuel or 10% RME fuel to power a test engine operated under three different  
518 conditions: engine-out (E/O), tailpipe-out (T.P/O), and regeneration (Regen).

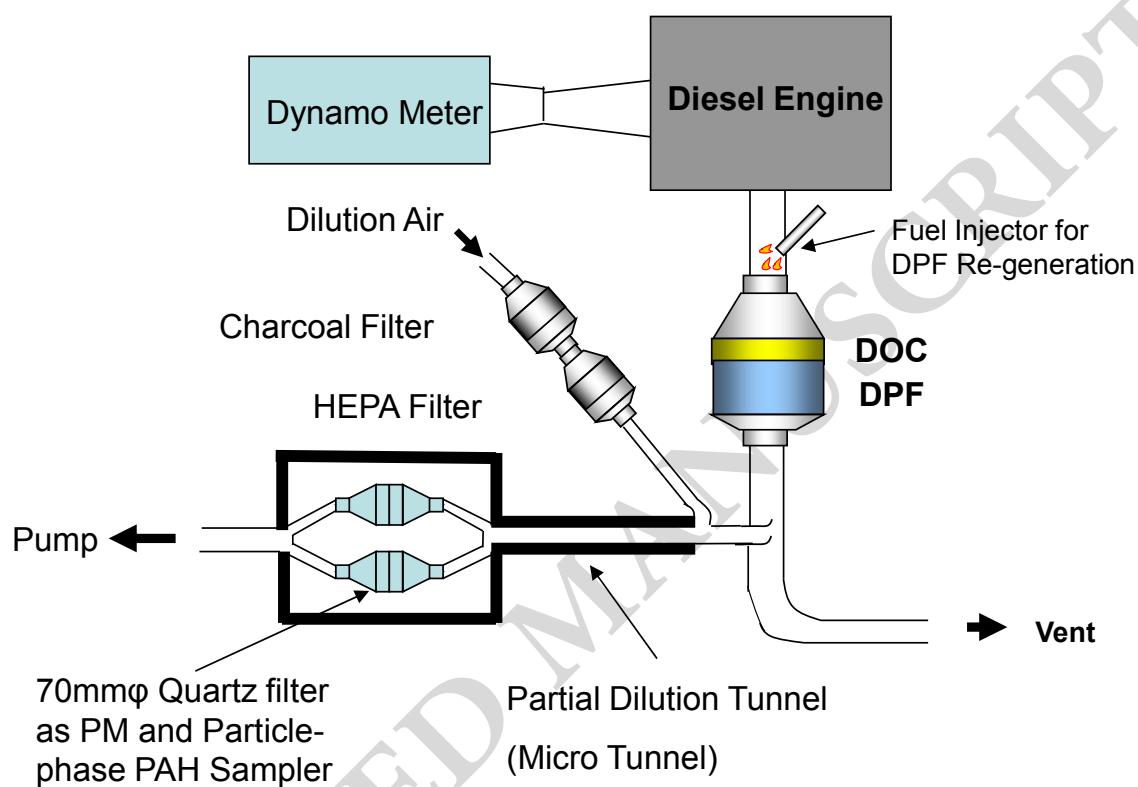
519 **Fig. 4.** Emissions of carbonaceous compounds, elemental carbon (EC) and organic carbon (OC)  
520 (upper graph) and particle-phase emissions of the three- to six-ringed polycyclic aromatic  
521 hydrocarbons (lower graph) associated with the use of petroleum diesel (D) fuel or 10% RME  
522 biodiesel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

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

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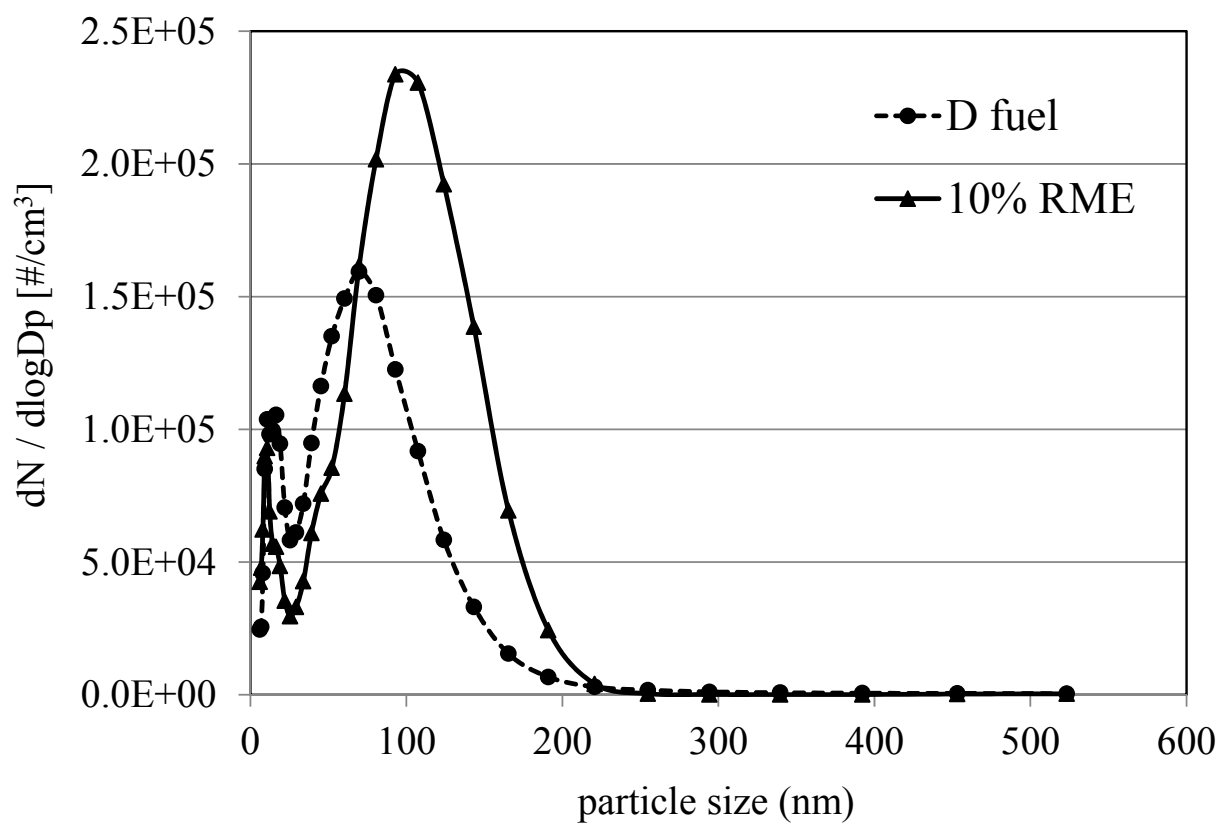
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**Fig. 1.**

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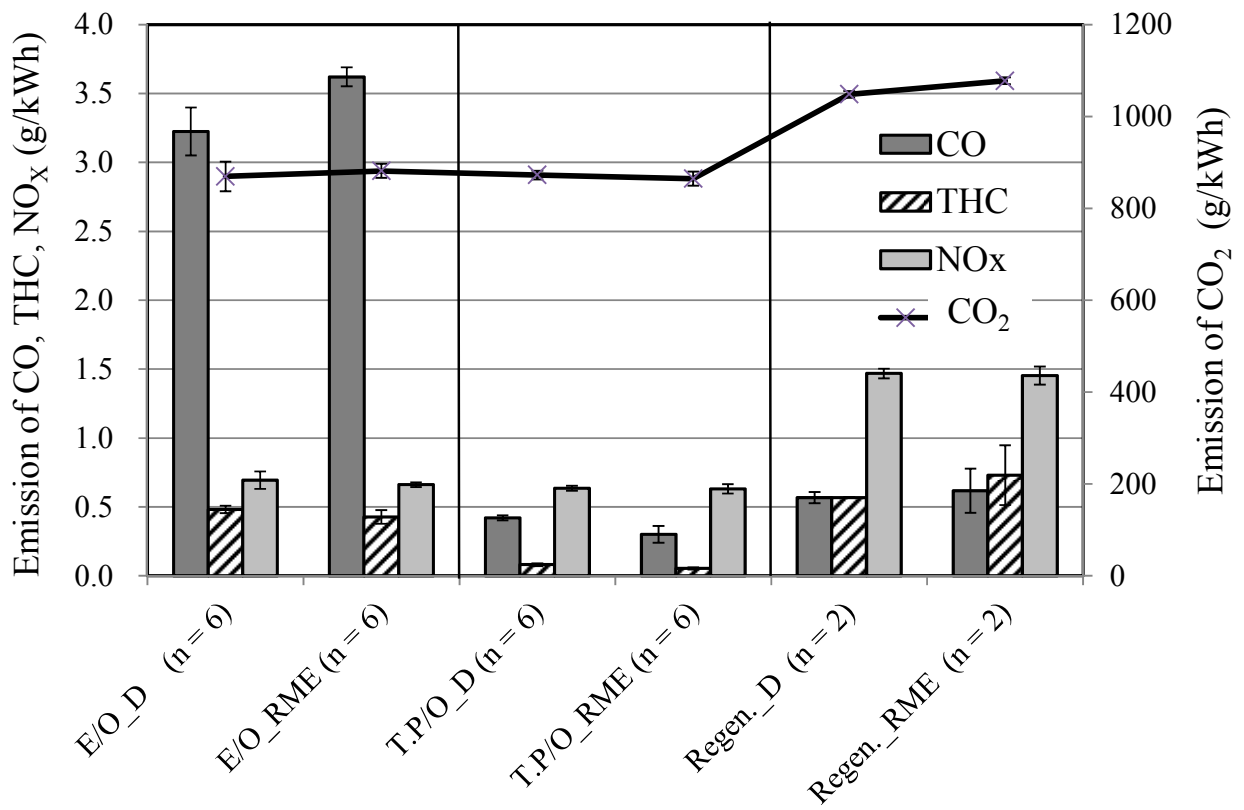
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Fig.2.



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**Fig.3.**

